IN THE UNITED STATES DISTRICT COURT
EASTERN DISTRICT OF TENNESSEE
AT CHATTANOOGA

ZECO, LLC, d/b/a ZEE COMPANY,	)	
	)	
Plaintiff/	)	No 1:21-cv-00079
Counterclaim Defendant	)	
v.	)	
	)	
ENVIRO TECH CHEMICAL	)	
SERVICES, INC.,	)	JURY TRIAL DEMANDED
	)	
Defendant/	)	
Counterclaimant	)	

AMENDED COMPLAINT FOR DECLARATORY JUDGMENT

This is a declaratory judgment action by Plaintiff, Zeco, LLC, d/b/a Zee Company, seeking a judicial declaration of non-infringement of U.S. Patent No. 10,912,321 (the "'321 patent"). A copy of the '321 patent is attached hereto as **Exhibit A**.

NATURE OF THIS ACTION

1. Defendant Enviro Tech Chemical Services, Inc. ("Enviro Tech") has been trying to threaten and to intimidate Plaintiffs' customers with insinuations that it infringes the '321 patent by purchasing products from Plaintiff. Enviro Tech has also threatened Plaintiff directly with allegations of infringement of the '321 patent. Enviro Tech seeks to threaten Plaintiff's business with its allegations of patent infringement. Enviro Tech's threats have created a definite and concrete justiciable controversy about the alleged infringement of the '321 patent. Accordingly, Plaintiff seeks a declaration that sales of products to its customers and its customers' use of those products do not constitute infringement of the '321 patent.

PARTIES

2. Plaintiff Zeco, LLC, d/b/a Zee Company (hereinafter "Zee Company') is limited liability company organized and existing under the laws of the State of Nevada, with a principal place of business at 412 Georgia Avenue, Suite 300, Chattanooga, TN 37403. Zee Company provides chemical applications to various industries. Zee Company has been a pioneer in providing chemical applications for manufacturing entities in the principal areas of the food and beverage industries, as well as the water and energy sectors. Zee Company holds numerous U.S. patents and pending U.S. patent applications relating to its proprietary technologies. Zee Company is a member company of the Vincit Group, an alliance of entities which provide a variety of goods and services to various manufacturing and processing industries, including but not limited to poultry, beef and pork processing facilities.

3. Defendant Enviro Tech Chemical Services, Inc., is a corporation organized and existing under the laws of the State of California, having a principal place of business at 500 Winmoore Way, Modesto CA 95358. Enviro Tech is a competitor of Zee Company, selling chemical products to the poultry processing industry.

JURISDICTION AND VENUE

4. The claims herein arise under the Declaratory Judgments Act, 28 U.S.C. §§ 2201, 2202 *et seq.* and the patent laws of the United States, 35 U.S.C. §§ 1 *et seq*.

5. This Court has subject matter jurisdiction based upon 28 U.S.C. §§ 1331, 1338(a), and 2201(a). This Court may declare the rights and other legal relations of the parties pursuant the provisions of the Declaratory Judgments Acts 28 U.S.C. §§ 2201 *et seq*. because this is a case of actual controversy within the Court's jurisdiction seeking a declaratory judgment that the '321 patent is not infringed. There exists a definite and concrete dispute within this Court's jurisdiction

between Plaintiff and Enviro Tech regarding the alleged infringement of the claims of the '321 patent, including for the reasons stated below, which authorizes this Court to provide a declaration of rights relating to Enviro Tech's allegations.

6. The Court has personal jurisdiction over Zee Company because Zee Company is a company that both has its principal place of business in Tennessee and does its business in the state.

7. The Court has personal jurisdiction over Enviro Tech because Enviro Tech has sent patent infringement letters to Plaintiff accusing Plaintiff of infringement. Enviro Tech sent those letters to Plaintiff's office in Chattanooga, Tennessee.

8. In 2016, Enviro Tech sent letters to numerous Zee Company customers claiming that the U.S. Patent and Trademark Office ("PTO") would soon be issuing a patent to Enviro Tech that might require Zee Company's customers to obtain a license to the patent to avoid infringement of it. A copy of such an exemplary letter is attached hereto as **Exhibit B**. The implication of the letter was that the purchase and use of peracetic acid ("PAA") from Zee Company to process poultry might cause Zee Company's customers to infringe the patent. It is unknown to what extent Enviro Tech continued to insinuate to Zee Company's customers thereafter that they might require a patent license from Enviro Tech because of the purchase and use of Zee Company's PAA.

9. After the issuance of the '321 patent earlier this year, Enviro Tech sent multiple letters to Plaintiff, via The Vincit Group, insinuating that Plaintiff required a license to the '321 patent. All of these letters were sent to Plaintiff's address in care of The Vincent Group on Georgia Avenue in Chattanooga, Tennessee. Copies of these three letters are attached hereto as **Exhibits C, D and E**.

10. On February 9, 2021, Enviro Tech wrote to The Vincit Group informing it of the issuance of the '321 patent. (**Exhibit C**.)

11. On February 23, 2021, Enviro Tech wrote to Plaintiff stating that it may have received notice of the issuance of the '321 patent, and that if Plaintiff was interested in obtaining a license to the '321 patent, to let Enviro Tech know. (**Exhibit D**.)

12. Plaintiff, through counsel, declined the offer to take a license to the '321 patent.

13. On March 30, 2021, Enviro Tech wrote to The Vincit Group again and copied Zee Company, informing the Vincit Group and Zee Company that "obtaining a license to perform the method of the '321 patent is not optional." Enviro Tech explicitly threatened to sue Plaintiff for patent infringement, stating that "as of May 1, 2021, we may be taking further steps in an effort to enforce our intellectual property rights." (**Exhibit E**.)

14. Upon information and belief, Enviro Tech wrote to Zee Company customers about the issuance of the '321 patent and threatened them with alleged infringement of the patent.

15. In addition to directing its threats to Plaintiff in the State of Tennessee, upon information and belief, Enviro Tech has in the past and still does sell chemical products directly or through distributors in Tennessee.

16. Thus, Enviro Tech has availed itself of the jurisdiction of this Court.

17. Venue is proper in this district pursuant to 28 U.S.C. § 1391(b) including for the same reasons set forth above.

THE '321 PATENT

18. The '321 patent is entitled "Methods of Using Peracetic Acid to Treat Poultry in a Chill Tank During Processing." It issued on February 9, 2021.

19. The ‘321 patent is based on a continuation-in-part of application number 13/065,553 filed on March 24, 2011.

20. The named inventors of the ‘321 patent are Michael S. Harvey and Jonathan N. Howarth.

21. The ‘321 patent is assigned to Enviro Tech.

22. The ‘321 patent claims a method for treating poultry by using PAA during processing in a very specific, step-wise, sequential fashion. In short, it is a method of treating poultry with an acid to increase the weight of the poultry and increase a processing plant’s yield of poultry production.

23. Claim 1 of the ‘312 patent, for example, reads as follows:

> A method of treating at least a portion of a poultry carcass with peracetic acid, said method comprising the steps of:
>
> providing, in a reservoir, a peracetic acid-containing water, wherein the peracetic acid-containing water comprises water and an antimicrobial amount of a solution of peracetic acid;
>
> after the step of providing the peracetic acid-containing water, determining the pH of the peracetic acid-containing water, and altering the pH of the peracetic acid-containing water to a pH of about 7.6 to about 10 by adding an alkaline source;
>
> after the step of determining the pH and altering the pH of the peracetic acid-containing water, placing into the peracetic acid-containing water at least a portion of a poultry carcass;
>
> after the step of placing at least the portion of the poultry carcass into the peracetic acid-containing water, determining the pH of the peracetic acid-containing water in the reservoir with at least the portion of the poultry carcass therein, and altering the pH of the peracetic acid-containing water to a pH of about 7.6 to about 10 by adding an alkaline source; and
>
> after the step of determining the pH and altering the pH of the peracetic acid-containing water having at least the portion of the poultry carcass therein, removing at least the portion of the poultry carcass from the peracetic acid-containing water.

24. All of the independent claims of the '321 patent recite the same steps, the only difference in the claims being the claimed pH ranges, with the pH range in claim 1 being the broadest.

THE NON-INFRINGEMENT OF THE '321 PATENT

25. There are two important principles relevant, for the purposes of this action, to the claims of the '321 patent.

26. First, the steps of the claims must be carried out in sequential order.

27. The sequential-order required is clear from the plain language of the claims themselves, which require the first recited step, then, "after [step 1]," only then step 2 be carried out, then "after [step 2]," only then step 3 be carried out, and so on.

28. The patent applicants agreed to this stepwise sequence of the claimed methods to overcome rejections by the patent examiner. By agreeing to this requirement, the applicants limited the scope of the claims by requiring that the steps be performed in sequential order.

29. The second important aspect of the claims for the purposes of this action is that the claimed methods require two pH adjustment steps: (1) determining the pH of the PAA-containing water solution and altering it with an alkaline source (*i.e.*, a base) ***before*** any poultry carcass is added to the solution; and (2) determining the pH of the solution and altering it ***after*** the poultry carcass is put into the solution.

30. Enviro Tech's threats to both Zee Company's customers and Plaintiff itself are frivolous because Zee Company does not recommend that its customers measure or adjust the pH of the solution in the poultry processing reservoir (known as a "chill tank") ***before*** the poultry carcass is put into it.

31. Instead, Zee Company instructs its customers to mix PAA and alkaline source with water to reach a desired pH ***outside of*** the chill tank before that resulting solution is introduced into the chill tank.

32. Thus, Zee Company does not instruct its customers to detect the pH of the processing solution in the chill tank before the poultry carcass is put into the chill tank.

33. Lest Enviro Tech intends to argue that any such measurement outside the chill tank, such as in a line into the chill tank, satisfies this requirement, Enviro Tech knows better. The patent claims make clear that the first measuring and pH adjustment step must be made inside the chill tank. Accordingly, any measurements outside the chill tank, such as in a line that runs into the chill tank, are not measurements covered by the patent claims.

34. Additionally, in a prior proceeding before the U.S. Patent and Trial Appeal Board, Defendant has asserted that the measurement and adjustment of the pH takes place in the chill tank. Patent applicants admitted as much during prosecution when they acknowledged to the U.lS. patent and Trial Appeal Board that the claimed reservoir is the reservoir into which the poultry is put, *i.e.*, the chill tank.

35. In an appeal brief, Defendant argued that "Dr. Howarth believes that a person skilled in the art of poultry processing in 2011 would not have found it obvious to adjust the pH of the [PAA] ***in the chill tank*** up at all, let alone up to the claimed alkaline ranges …." (emphasis added.)

36. Defendant's representative further stated during the oral hearing on the appeal that:

> So the steps of the method are, as I said, are the same except for the pH range. The [PAA] is provided ***in the chill tank***. The pH is determined. An alkaline source which is usually sodium hydroxide is added ***to the chill tank*** to raise the pH to the specified alkaline range. The poultry is then added. The pH is then determined again and the alkaline source is the same one is added again to maintain the pH at

> the same range that was selected and or course at the end, the poultry is removed from the chill tank.

(emphasis added.)

37. Upon information and belief, Enviro Tech knows that Zee Company does not instruct its customers to use its PAA to measure the pH of solution before any poultry carcass is put into the chill tank, much less measure and then make any adjustment to the pH by adding alkaline source to the chill tank.

38. Enviro Tech has never explained to either Zee Company's customers, as far as Plaintiff knows, or to Plaintiff itself how Plaintiff, whether directly or indirectly, could be infringing the '321 patent in view of these obvious reasons of non-infringement.

39. Plaintiff avers that additional bases exist that establish that Plaintiff does not infringe the '321 patent. These reasons are set forth herein are mere exemplars of the baselessness of Enviro Tech's threats of patent infringement.

40. Defendant represented to the USPTO that almost the entire poultry processing industry performed its claimed invention prior to issuance of the '312 patent.

41. During the prosecution of the '321 patent, Defendant's representative submitted a Reply to Office Action, dated February 19, 2019, which provided the following:

> Applicant's claimed method of adjusting the pH in the chill tanks to an alkaline pH of 7.6-10 by adding an alkaline chemical is now almost uniformly adopted throughout the U.S. poultry processing industry. The method is being used by almost all poultry processing plants.

(emphasis in original).

42. During the prosecution of the '312 patent, Defendant's representative submitted a declaration of Brett Sutton, signed January 22, 2019, which provided the following:

> We have visited a lot of poultry processing plants throughout the U.S. Based on our experience, I believe about 90% of the poultry processing industry' uses

> peracetic acid in their chill tanks, and about 99% of those companies use Enviro Tech's pH adjustment method. We are not aware of any plant using peracetic acid that does not use pH adjustment.

(emphasis added.)

43. During prosecution of the '312 patent, Defendant's representative submitted a declaration of Brent Lundstrum, signed February 14, 2019, which provided the following:

> Of all of the poultry processing plants that I know are using peracetic add in their chill tanks, all of them are adjusting the pH up to an alkaline pH by adding an alkaline chemical.

44. During prosecution of the '312 patent, Defendant's representative submitted a declaration of Charles Johnson, signed January 22, 2019, which provided the following:

> I would he surprised if there are any poultry processing companies in the U.S. that are not using Enviro Tech's pH adjustment method to adjust the pH of the peracetic acid in their chill tanks.

45. During prosecution of the '312 patent, Defendant's representative submitted a declaration of Brian Golbus, signed January 21, 2019, which provided the following:

> Since Enviro Tech developed its pH adjustment method, all of the management I've spoken to and all of the plants I 've visited that are using peracetic acid in their chill tanks are adjusting the pH up to an alkaline pH by adding an alkaline chemical.

THE INVALIDITY OF THE '321 PATENT

46. PAA's acid-base chemistry, including its pKA of 8.2 at 25 ºC, was known in the art before the '321 patent's alleged invention date and effective filing date.

47. PAA has been sold by Enviro Tech and others, whether directly or indirectly through distributors, to poultry processors for use in poultry processing facilities as an antimicrobial treatment since at least the mid-2000s and before the '321 patent's alleged invention date and effective filing date.

48. Before the '321 patent's alleged invention date and effective filing date, commercial PAA products typically had PAA concentrations of about 1-15% w/w, although concentrations of up to 30% were possible.

49. Before the '321 patent's alleged invention date and effective filing date, Enviro Tech made or sold PAA products, including formulations with 6% and 15% PAA.

50. Poultry processors are regulated by the Food Safety Inspection Service (FSIS), which is part of the United States Department of Agriculture (USDA).

51. Poultry processors were regulated by the FSIS before the '321 patent's alleged invention date and effective filing date.

52. On information and belief, Enviro Tech is not a poultry processor.

53. On information and belief, Enviro Tech has never been a poultry processor.

54. On information and belief, Enviro Tech does not operate any poultry processing facility.

55. On information and belief, Enviro Tech has not ever operated a poultry processing facility.

56. Before the '321 patent's alleged invention date and effective filing date, poultry processors purchased live poultry for processing.

57. Before the '321 patent's alleged invention date and effective filing date, poultry processors processed live poultry delivered to poultry processing facilities.

58. Before the '321 patent's alleged invention date and effective filing date, poultry processors hung poultry to shackle conveyors.

59. Before the '321 patent's alleged invention date and effective filing date, poultry processors slaughtered and exsanguinated live poultry.

60. Before the '321 patent's alleged invention date and effective filing date, poultry carcasses deemed by officials of USDA as sufficiently healthy and free of fecal and digestive tract matter were conveyed into chill tanks.

61. Chill tanks have been known and used by poultry processors in poultry processing facilities for decades.

62. Chill tanks were known and used by poultry processors in poultry processing facilities before the '321 patent's alleged invention date and effective filing date.

63. FSIS regulated poultry processors' use of chill tanks in poultry processing facilities before the '321 patent's alleged invention date and effective filing date.

64. Before the '321 patent's alleged invention date and effective filing date, Enviro Tech made and sold PAA products for use in chill tanks in poultry processing facilities.

65. Before the '321 patent's alleged invention date and effective filing date, poultry processors would fill chill tanks with water to cool poultry carcasses before further processing.

66. Before the '321 patent's alleged invention date and effective filing date, poultry processors would fill chill tanks with water and add an antimicrobial agent, like the PAA products Enviro Tech made and sold.

67. Before the '321 patent's alleged invention date and effective filing date, poultry processors would fill chill tanks with water and an antimicrobial agent, like PAA, before introducing any poultry carcasses into the chill tanks.

68. Before the '321 patent's alleged invention date and effective filing date, poultry processors would introduce poultry carcasses into chill tanks, move the carcasses through chill tanks by means of an auger, and determine the residence time in the chill tanks based on the type of poultry.

69. Before the '321 patent's alleged invention date and effective filing date, poultry processors would remove carcasses from chill tanks for further processing or packaging.

70. Before the '321 patent's alleged invention date and effective filing date, the FSIS must approve any antimicrobial agent that contacts poultry, like the PAA products Enviro Tech has sold, prior to use with poultry carcasses.

71. Before the '321 patent's alleged invention date and effective filing date, PAA was an approved antimicrobial agent in poultry processing.

72. Before the '321 patent's alleged invention date and effective filing date, measuring, controlling, and altering the pH of antimicrobial-containing water in chill tanks were known in the art.

73. Attached as **Exhibit F** is a true and correct copy of. U.S. Patent. No. 6,605,253 which issued August 12, 2003, to Perkins (the "Perkins patent"). **Exhibit F** is hereby incorporated by reference.

74. The Perkins patent, which issued August 12, 2003, describes a process for monitoring, controlling, and altering the pH at a desired level during poultry processing, including in a chiller tank. (**Exhibit F**, Abstract.)

75. The Perkins patent is prior art to the '321 patent.

76. Enviro Tech's expert consultant, Dr. Josh Herring, Ph.D, stated the following:

> 38. Also discussed in more detail below, the claims do not require any specific method of determining the pH of the PAA-containing water. For example, when discussing monitoring the pH, the specification states that pH may be determined by "any method," ***and lists examples of both direct and indirect industry standard methods***. (Ex. B at 34:32-34.)
>
> 39. The specification discloses embodiments of this ***method useful in large commercial operations.*** For example, the '321 patent discloses that the method may be performed continuously, ***as it was done previously with chlorine-based antimicrobial interventions, and that the method may be automated***.

…

> (Ex. B at 37:63-38:16). This is consistent with my experience through the poultry slaughter/processing industry, product development and meat product production, and even fermented beverage industry.

(ECF 61-1, ¶¶ 38-39 (emphasis added).)

77. The citations to "Ex. B" refers to the '321 patent.

78. Dr. Herring also stated that he "obtained a B.S. in Animal and Dairy Sciences Pre-Veterinary Medicine from Auburn University in 1998." (ECF 61-1, ¶ 9.)

79. Dr. Herring stated that he "then attended graduate school at Mississippi State University, where I obtained an M.S. in Food Science and Technology in 2002 and a Ph.D. in Food Science and Technology in 2004, with a major emphasis in Meat Science and a Minor in Microbiology." (ECF 61-1, ¶ 9.)

80. Dr. Herring stated the following:

> I have a unique perspective on the poultry industry, as, unlike many academics, I have practical experience working in poultry processing plants. ***Prior to my graduate studies, I was employed by Gold Kist Inc. At Gold Kist Inc., I was a Line Supervisor at the Trussville, AL Gold Kist poultry processing plant***. As the Line Supervisor I was responsible for KFC (Kentucky Fried Chicken) cut up. ***Part of my duties in this position was to monitor water temperature***, product temperature, ***and pH as out-of-compliance processing required rework of products***.

(ECF 61-1, ¶ 11 (emphasis added).)

81. The above-identified statements from Enviro Tech's expert consultant Dr. Herring are prior art.

82. Before the '321 patent's alleged invention date and effective filing date, the antimicrobial efficacy of PAA or PAA-related chemicals in alkaline pH ranges, including at a pH of 8.0, were known in the art.

83. Attached as **Exhibit G** is a true and correct copy of U.S. Provisional Appl. No. 61/427,965 to Li et al. (the "Li provisional"), filed December 29, 2010, including the cover sheet and filing receipt. **Exhibit G** is hereby incorporated by reference in its entirety. Attached as **Exhibit H** is a true and correct copy of U.S. Patent No. 8,877,254 to Li et al. (the "Li patent"), which issued November 4, 2014, and claimed priority to the Li provisional**. Exhibit H** hereby incorporated in its entirety. Together, the Li provisional and Li patent will be referred to as the "Li provisional and patent."

84. The Li provisional and patent provide that "peroxyacetic acid" is the "most commonly used peroxycarboxylic acid." (**Exhibit G**, at 7/62; **Exhibit H**, col. 1, ll. 47-49.)

85. The Li provisional and patent provide methods for forming peroxycarboxylic acid compositions. (**Exhibit G**, at 9/62; **Exhibit H**, col. 2, l. 63-col. 3, l. 15.)

86. The Li provisional and patent describe diluting such compositions to a pH of about 8.0. (**Exhibit G**, at 9/62, 30/62; **Exhibit H**, col. 2, l. 63-col. 3 l. 15.)

87. The Li provisional and patent define "poultry." (**Exhibit G**, at 13/62; **Exhibit H**, col. 8, ll. 35-54.)

88. The Li provisional and patent provide that the disclosed "compositions may also be used to treat animal carcasses to reduce both pathogenic and non-pathogenic microbial levels." (**Exhibit G**, at 36/62; **Exhibit H**, col. 26, ll. 33-35.)

89. The Li provisional and patent are prior art to the '321 patent.

90. Attached as **Exhibit I** is a true and correct copy of U.S. Patent No. 5,200,189 to Oakes et al (the "Oakes patent"), which issued April 6, 1993. **Exhibit I** is hereby incorporated by reference in its entirety.

91. The Oakes patent provides a "peroxyacid antimicrobial concentrate and use composition is provided comprising a C1 to C4 peroxycarboxylic acid, and a C6 to C18 peroxyacid." (**Exhibit I,** Abstract.)

92. The Oakes patent provides that an "effective antimicrobial use solution is formed at low concentrations when the concentrate composition is diluted with water to a pH in the range of about 2 to 8." (**Exhibit I,** Abstract.)

93. The Oakes patent is prior art to the '321 patent.

94. Before the '321 patent's alleged invention date and effective filing date, it was known in the art to use chemicals at an alkaline pH to improve moisture retention and reduce microbial growth.

95. Attached as **Exhibit J** is a true and correct copy of *Marination to Improve Functional Properties and Safety of Poultry Meat* by C. Alvardo and S. McKee, published March 2007 in the Journal of Applied Poultry Research, (the "Alvarado publication"). **Exhibit J** is hereby incorporated by reference in its entirety.

96. The Alvarado publication relates to poultry and "water-holding capacity (**WHC**)." (**Exhibit J**, at 114 (emphasis in original).)

97. The Alvarado publication provides that a "factor influencing water binding is meat pH." (**Exhibit J**, at 114.)

98. The Alvarado publication provides the following:

> Decreased WHC is even more evident in meat from animals that have accelerated postmortem metabolism after slaughter. ***Research has indicated that the low pH resulting from rapid metabolism early postmortem when combined with high carcass temperatures causes extensive protein denaturation in the muscle, thereby affecting meat quality characteristics [15, 16, 17, 18].*** The loss of protein functionality due to extensive protein denaturation is considered to be the primary factor associated with the development of pale, soft, and exudative (**PSE**) meat characteristic [16, 19, 20, 21]. When meat conditions such as PSE meat

exist, the WHC and other meat quality characteristics are further compromised because of the extensive protein denaturation. ***Differences in WHC, brine pickup, and retention have been reported to vary with fillet color and initial fillet pH [22, 23]. Alvarado and Sams [22] and Woelfel and Sams [23] compared brining and WHC of broiler breast fillets characterized as "pale" fillets to fillets characterized as "normal." Their findings suggested that the fillet color and pH were highly correlated with WHC and percentage of brining pickup and retention***. Fillet characterized as lighter in color had an initial lower pH, lower brine pickup, and higher drip and cook loss compared with fillets that were characterized as dark.

(**Exhibit J**, at 115 (bold emphasis in original; bold italics emphasis added; line break hyphens from publication not included).)

99. The Alvarado publication provides the following:

When phosphates are used for increasing water-holding properties of meat, the USDA requires that phosphate concentrations are no higher than 0.5% of the finished product weight. Although there are many phosphates to choose from, STP remains the most commonly utilized in brine solutions because it is easy to use and inexpensive. Sodium tripolyphosphate accounts for approximately 80% of the phosphates used in further-processed meat products. Other commonly used phosphates include sodium pyrophosphate and sodium hexametaphosphate (**SHMP**). ***Alkaline phosphates such as STP serve to increase WHC, increase cook yield, extract muscle proteins, reduce oxidative rancidity, preserve meat color, increase flavor retention, and reduce microbial growth [26].***

(**Exhibit J**, at 116 (bold emphasis in original; bold italics emphasis added; line break hyphens from publication not included).)

100. The Alvarado provides the following:

Today, blends are becoming more popular based on their solubility and functionality in a variety of meat product formulations. Sodium SHMP is a water-soluble form of sodium phosphate that is also known as Graham's salt. How-ever, the solubility of SHMP is not as good as other tripolyphosphates, so the phosphate can be blended with others, giving better solubility properties. For example, blends including SHMP combined with tripolyphosphate improve the solubility of SHMP. ***Desirable properties for blends include proper alkaline pH,*** good solubility, ability to hydrolyze to form diphosphate, Ca compatibility, the ability to solubilize myofibrillar proteins, and the ability to expose charged binding sites ***to increase WHC [28].***

(**Exhibit J**, at 116 (emphasis added; line break hyphens from publication not included).)

101. The Alvarado publication is prior art to the '321 patent.

102. According to Enviro Tech's expert consultant, Dr. Josh Herring, Ph.D., a person of ordinary skill in the art would have been a person with a bachelor's degree in a relevant field with 5-7 years of experience, a master's degree in the relevant field with 3-5 years of experience, or a Ph.D. in a relevant field. (ECF 61-1, ¶ 41.)

103. A highly-skilled person of ordinary skill in the art, like the one asserted by Dr. Herring, would have either known all limitations of the '321 patent's claimed invention, including those of claim 1, before the '321 patent's alleged invention date or effective filing date or the limitations would have been obvious at the time of invention, as, for example, the application of things known in the art to yield predictable results.

104. Enviro Tech's commercial activities before filing the '321 patent and statements constitute prior art to the '321 patent under pre-AIA 35 U.S.C. §§ 102-103 and are indicative of both the scope and content of the prior art and what was known in the art before the '321 patent's alleged invention date and effective filing date.

105. On information and belief, statements in the '321 patent, including those in the "Background of the Invention," rely on the known, public, or commercial activities of Enviro Tech or others, including downstream poultry processing facilities, activities that occurred before the '321 patent's alleged invention date or effective filing date.

106. Various publications, patents, and commercial activities, including those referenced above, constitute prior art to the '321 patent under pre-AIA 35 U.S.C. §§ 102-103 and are indicative of both the scope and content of the prior art and what was known in the art before the '321 patent's alleged invention date and effective filing date.

107. Regarding the preamble of claim 1 of the ‘321 patent, to the extent it is limiting, methods of treating at least a portion of a poultry carcass with peracetic acid were known in the art or obvious to one of ordinary skill in the art before the ‘321 patent’s alleged invention date or effective filing date, as reflected in the prior art referenced in Paragraphs 46 – 106.

108. Regarding the first recited step of claim 1 of the ’321 patent, providing, in a reservoir, a peracetic acid-containing water, wherein the peracetic acid-containing water comprises water and an antimicrobial amount of a solution of peracetic acid was either known in the art before the ‘321 patent’s alleged invention date or effective filing date or would have been obvious to one of ordinary skill in the art at the alleged time of invention, as reflected in the prior art referenced in Paragraphs 46 – 107.

109. Regarding the second recited step of claim 1 of the ’321 patent, after the step of providing the peracetic-acid containing water, determining the pH of the peracetic acid-containing water, and altering the pH of the peracetic acid-containing water to a pH of about 7.6 to about 10 by adding an alkaline source was either known in the art before the ‘321 patent’s alleged invention date or effective filing date or would have been obvious to one of ordinary skill in the art at the alleged time of invention, as reflected in the prior art referenced in Paragraphs 46 – 108.

110. Regarding the third recited step of claim 1 of the ‘321 patent, after the step of determining the pH and altering the pH of the peracetic acid-containing water, placing into the peracetic acid-containing water at least a portion of a poultry carcass was either known in the art before the ‘321 patent’s alleged invention date or effective filing date or would have been obvious to one of ordinary skill in the art at the alleged time of invention, as reflected in the prior art referenced in Paragraphs 46 – 109.

111. Regarding the fourth recited step of claim 1 of the '321 patent, after the step of placing at least the portion of the poultry carcass into the peracetic acid-containing water, determining the pH of the peracetic acid-containing water in the reservoir with at least the portion of the poultry carcass therein, and altering the pH of the peracetic acid-containing water to a pH of about 7.6 to about 10 by adding an alkaline source was either known in the art before the '321 patent's alleged invention date or effective filing date or would have been obvious to one of ordinary skill in the art at the alleged time of invention, as reflected in the prior art referenced in Paragraphs 46 – 110.

112. Regarding the fifth recited step of claim 1 of the '321 patent, after the step of determining the pH and altering the pH of the peracetic acid-containing water having at least the portion of the poultry carcass therein, removing at least the portion of the poultry carcass from the peracetic acid-containing water was either known in the art before the '321 patent's alleged invention date or effective filing date or would have been obvious to one of ordinary skill in the art at the alleged time of invention, as reflected in the prior art referenced in Paragraphs 46 – 111.

COUNT I: DECLARATORY JUDGMENT OF NON-INFRINGEMENT

113. Plaintiff hereby realleges and incorporates by reference, as if fully set forth herein, the allegations of paragraphs 1– 45 above.

114. For the reasons set forth in this Complaint, there exists an actual case or controversy between Plaintiff and Enviro Tech because of Enviro Tech's actions and threats.

115. Plaintiff is entitled to make and sell PAA according to the instructions provided by Zee Company to its customers, insofar as neither Plaintiff directly nor indirectly infringes any claim of the '321 patent, including, but not limited to, for the reasons set forth herein.

116. Neither Plaintiff infringes any claim of the '321 patent literally or under the doctrine of equivalents.

117. Because a definite and concrete dispute exists between the parties regarding the alleged infringement of the '321 patent, this Court should issue a judicial declaration that Plaintiff does not infringe any claim of the '321 patent.

COUNT II: DECLARATORY JUDGMENT OF INVAVLIDITY

118. Plaintiff hereby realleges and incorporates by reference, as if fully set forth herein, the allegations of paragraphs 1 – 112 above.

119. For the reasons set forth in this Complaint, there exists an actual case or controversy between Plaintiff and Enviro Tech because of Enviro Tech's actions and threats.

120. The '321 patent is invalid for failure to meet the conditions of patentability, including those specified in pre-AIA 35 U.S.C. § 103.

121. Plaintiff is entitled to a declaration that the claims of the '321 patent are invalid.

PRAYER FOR RELIEF

WHEREFORE, Plaintiff respectfully requests that the Court enter judgment in favor of Plaintiff as follows:

A. Finding that Plaintiff does not infringe any claim of the '321 patent, whether literally or under the doctrine of equivalents, or whether directly or indirectly, or in any other respect under 35 U.S.C. § 271;

B. Finding that the allegations of infringement of the '321 patent made by Enviro Tech are baseless;

C. Enjoining Enviro Tech, and all persons in active concert or participation with Enviro Tech, either directly or indirectly, from charging infringement of, or instituting any action for

infringement of, the '321 patent against Plaintiff, its vendors, its business partners, its distributors, or its customers for the manufacture, sale, use, offer for sale, or importation of PAA;

D. Finding that each claim of the '321 patent is invalid;

E. Awarding Plaintiff costs, expenses, and its attorney fees pursuant to 35 U.S.C. § 285, Rule 54(d) of the Federal Rules of Civil Procedure, and any other applicable statute or rule, or the inherent authority of the Court; and

F. Awarding Plaintiff such other and further relief as the Court deems just, equitable and proper.

Dated: August 26, 2022

/s/ Adam E. Szymanski

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US006605253B1

(12) **United States Patent**
Perkins

(10) **Patent No.: US 6,605,253 B1**
(45) **Date of Patent: Aug. 12, 2003**

(54) **INTERVENTION TECHNIQUES FOR REDUCING CARCASS CONTAMINATION**

(75) Inventor: **Michael Perkins**, Poquoson, VA (US)

(73) Assignee: **Zentox Corporation**, Boston, MA (US)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 237 days.

(21) Appl. No.: **09/591,513**

(22) Filed: **Jun. 9, 2000**

Related U.S. Application Data

(60) Provisional application No. 60/138,368, filed on Jun. 10, 1999.

(51) **Int. Cl.**[7] **A61L 9/00**; B01J 19/08; C02F 1/76; B01D 1/00; A21D 4/00

(52) **U.S. Cl.** **422/28**; 422/31; 422/32; 422/34; 422/37; 422/79; 422/186.07; 210/752; 210/756; 210/760; 210/704; 210/724; 210/905; 426/320; 426/321; 426/326; 426/332; 426/335

(58) **Field of Search** 422/1, 6, 28–37, 422/38, 41, 79, 101, 119, 121, 123, 186.07, 186.1, 186.12, 186.21, 256, 261, 292, 301, 305–307; 210/752, 754, 756, 760, 764, 704, 905, 724–725; 426/320–321, 326, 332, 335

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Primary Examiner—Robert J. Warden, Sr.
Assistant Examiner—Monzer R. Chorbaji
(74) *Attorney, Agent, or Firm*—John C. Serio; Brown Rudnick Berlack Israels LLP

(57) **ABSTRACT**

The presently disclosed disinfection process for use in the processing of foodstuffs is designed as an intervention step in poultry processing to allow for continuous on-line processing of poultry carcasses that may have accidentally become contaminated during the evisceration process. Such on-line processing is designed to replace the need for off-line manual washing and cleaning of the contaminated carcasses. By eliminating such off-line manual washing, food safety will be enhanced due to the elimination of the physical handling of carcasses and the cross-contamination that may result from such physical handling. An additional benefit is that the production process will also be able to run with a reduced number of interruptions, which will result in a more efficient production process. The invention described herein is designed to employ the advantages of controlled chlorination at optimum pH levels, together with the proven effectiveness of increased contact time through the implementation of multiple stage treatment of the carcasses during slaughter, evisceration, washing and chilling. Additionally, an improved device and method are provided for effecting economic and efficient regulation of disinfection agent effectiveness, comprising a system and method for removing a major portion of filterable materials, represented as total chemical oxidation demand from the chiller tank water.

15 Claims, 4 Drawing Sheets

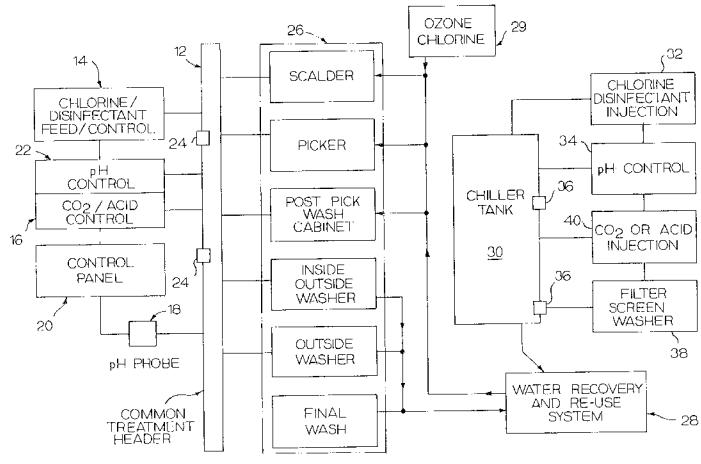

EXHIBIT F

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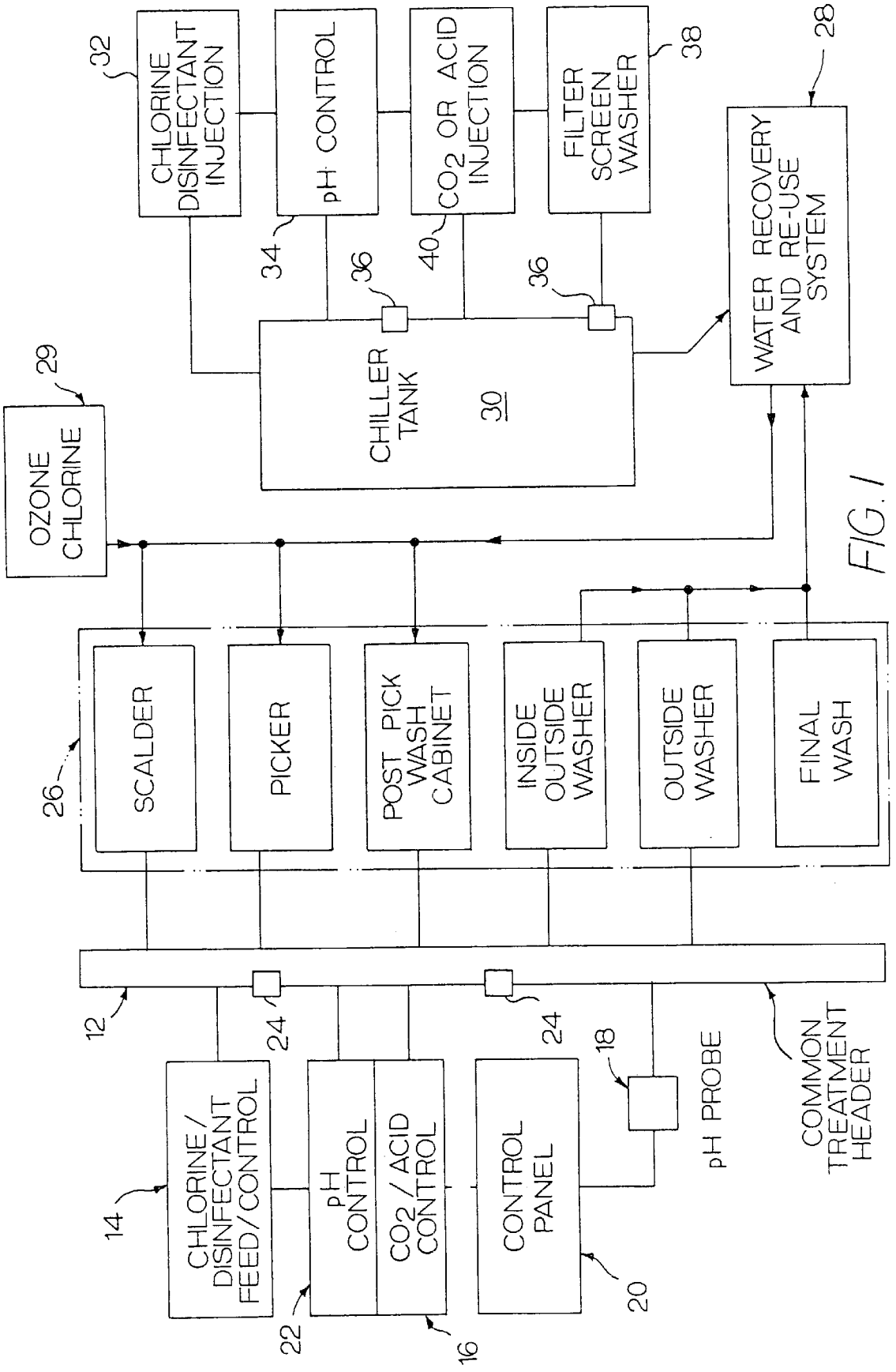
32
CHLORINE DISINFECTANT INJECTION
pH CONTROL
CO_2 OR ACID INJECTION
FILTER SCREEN WASHER
38
28
WATER RECOVERY AND RE-USE SYSTEM
34
36
40
36
CHILLER TANK
30
29
OZONE CHLORINE
26
SCALDER
PICKER
POST PICK WASH CABINET
INSIDE OUTSIDE WASHER
OUTSIDE WASHER
FINAL WASH
12
24
24
18
pH PROBE
COMMON TREATMENT HEADER
14
CHLORINE / DISINFECTANT FEED/CONTROL
pH CONTROL
CO_2 / ACID CONTROL
CONTROL PANEL
22
16
20

FIG. 1

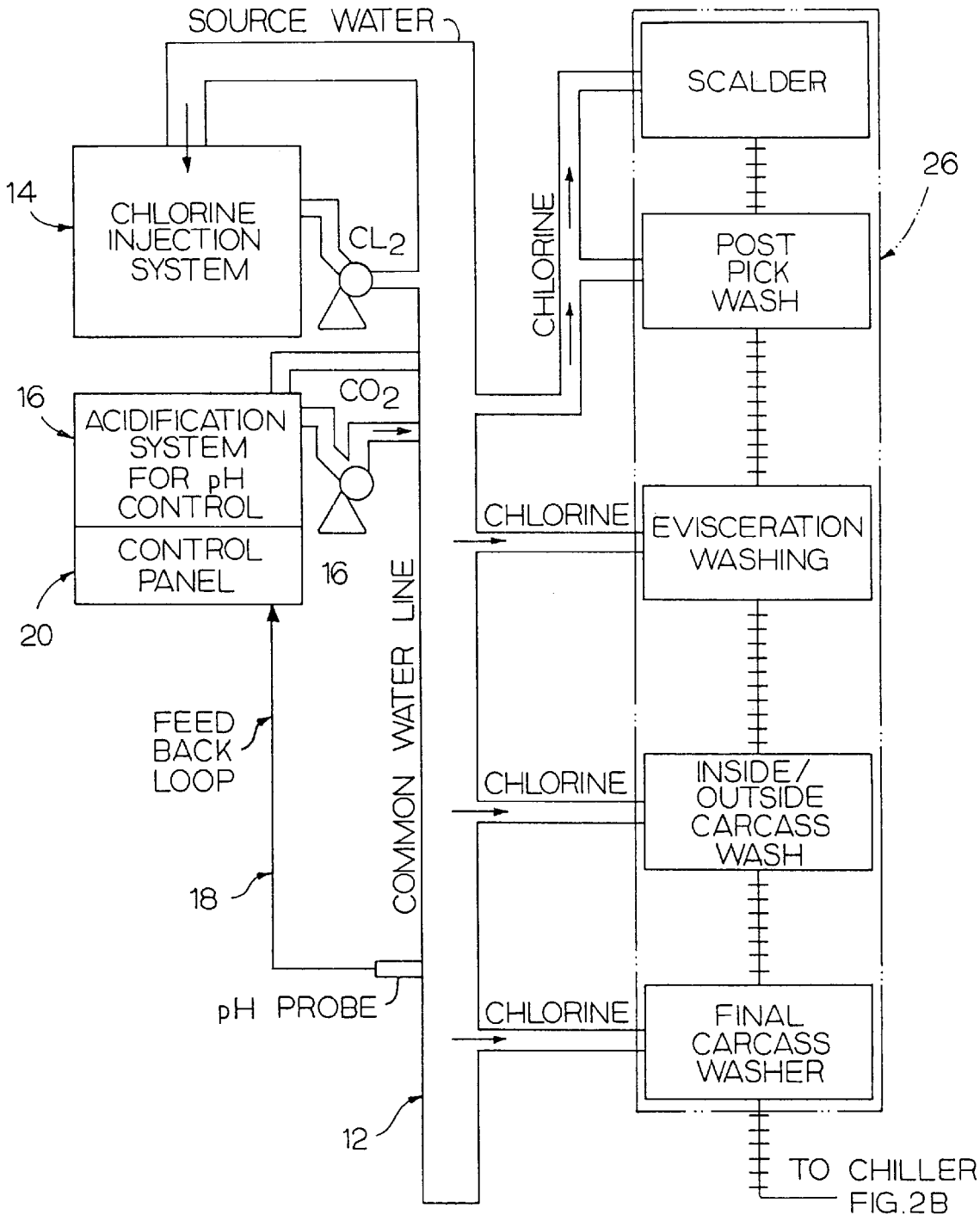
SOURCE WATER
SCALDER
26
14
CHLORINE INJECTION SYSTEM
CL_2
CHLORINE
POST PICK WASH
16
ACIDIFICATION SYSTEM FOR pH CONTROL
CO_2
CHLORINE
EVISCERATION WASHING
CONTROL PANEL
16
20
COMMON WATER LINE
FEED BACK LOOP
CHLORINE
INSIDE/ OUTSIDE CARCASS WASH
18
pH PROBE
CHLORINE
FINAL CARCASS WASHER
12
TO CHILLER FIG.2B

FIG. 2A

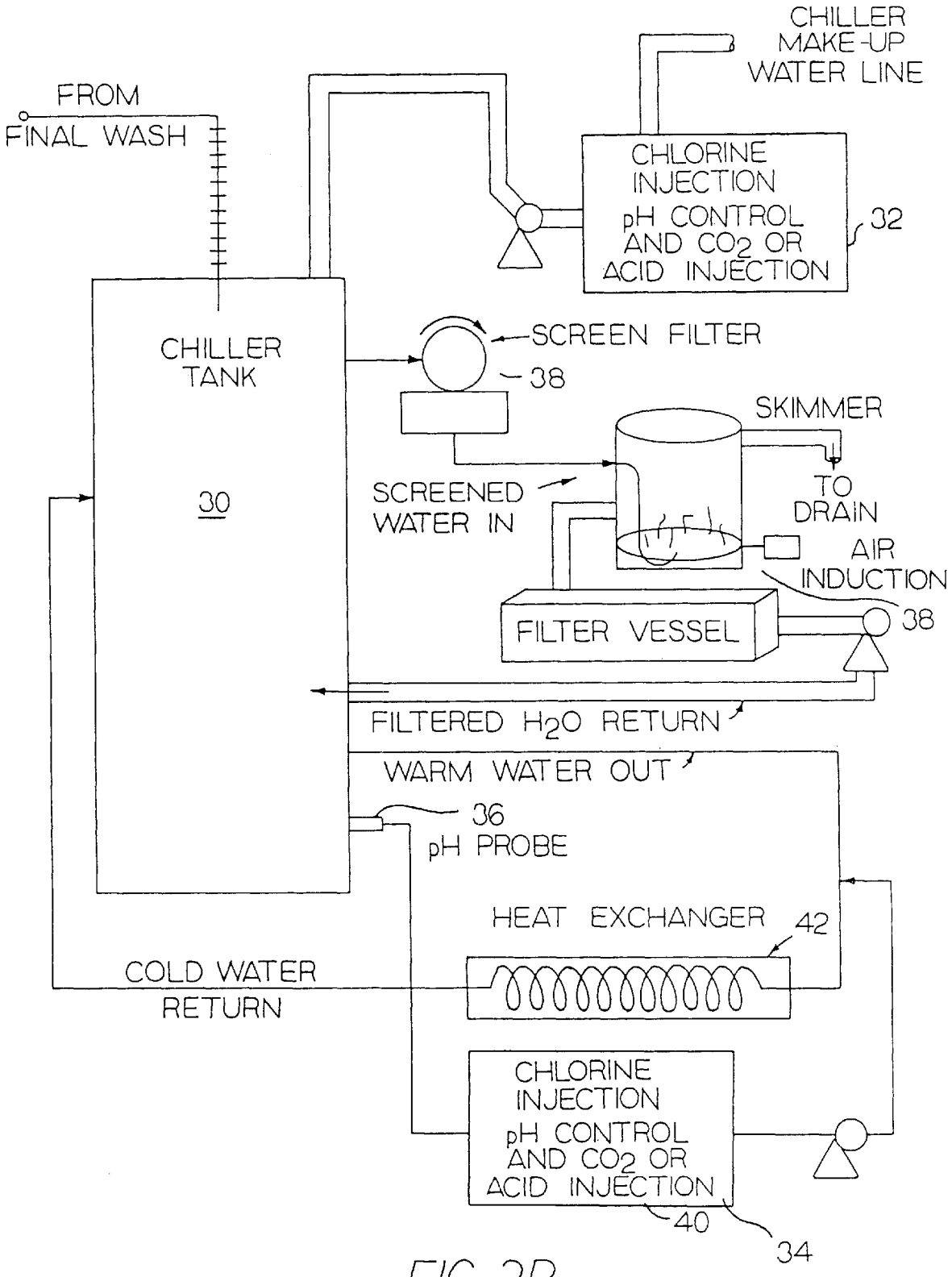
CHILLER MAKE-UP WATER LINE
FROM FINAL WASH
CHLORINE INJECTION pH CONTROL AND CO_2 OR ACID INJECTION
32
CHILLER TANK
30
SCREEN FILTER
38
SKIMMER
SCREENED WATER IN
TO DRAIN
AIR INDUCTION
FILTER VESSEL
38
FILTERED H_2O RETURN
WARM WATER OUT
36
pH PROBE
HEAT EXCHANGER
42
COLD WATER RETURN
CHLORINE INJECTION pH CONTROL AND CO_2 OR ACID INJECTION
40
34

FIG. 2B

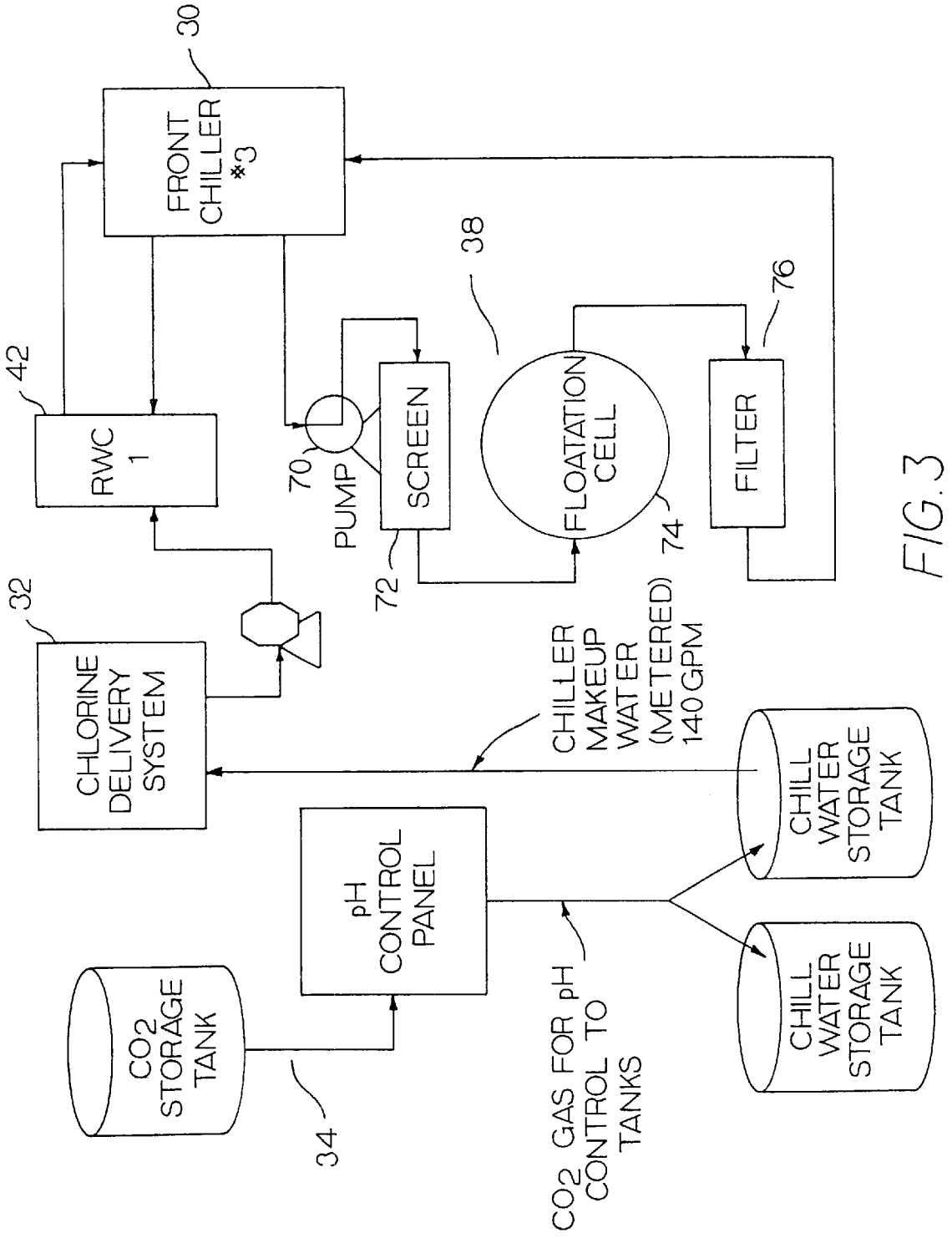
30
FRONT CHILLER #3
38
76
42
RWC 1
70
PUMP
SCREEN
FLOATATION CELL
FILTER
72
74
32
CHLORINE DELIVERY SYSTEM
CHILLER MAKEUP WATER (METERED) 140 GPM
CHILL WATER STORAGE TANK
pH CONTROL PANEL
CHILL WATER STORAGE TANK
CO2 STORAGE TANK
34
CO2 GAS FOR pH CONTROL TO TANKS

FIG. 3

INTERVENTION TECHNIQUES FOR REDUCING CARCASS CONTAMINATION

CROSS-REFERENCE TO RELATED APPLICATIONS

This Patent Application claims the benefit of U.S. Provisional Application No. 60/138,368 filed Jun. 10, 1999, the contents of which are incorporated herein by reference in its entirety.

BACKGROUND

1. Technical Field

The present disclosure relates generally to the field of carcass processing, and particularly, is directed to an enhanced water disinfection process for use in the processing of a foodstuffs. More particularly, the disinfection process is designed as an intervention step in poultry processing to allow for continuous on-line processing of poultry carcasses that may have accidentally become contaminated during the evisceration process.

2. Background of the Related Art

The typical poultry processing plant receives live animals from the grow-out farms, slaughters the animals, drains the blood and then removes the feathers, "paws", heads and eviscera in the initial stages of processing. The carcasses are thereafter sent by way of mechanized line operations through a series of washing, chilling and sanitizing steps before the product is shipped as "fresh" product or packaged for freezing. These line operations typically consume large quantities of water.

Accordingly, the poultry processing industry has generally been characterized as a large volume consumer of water in conducting the slaughter, processing, and packing of the animals for both human consumption and other uses. Recent initiatives by the United States Department of Agriculture (USDA), under the jurisdiction of the Food Safety Inspection Service (FSIS), have resulted in a further increase in the volume of water used to wash poultry carcasses in order to meet the more stringent requirements of zero (0) tolerance for visible fecal contamination. Furthermore, recent introduction of Hazardous Analysis and Critical Control Point (HACCP) programs provide for the transition of the inspection process from one heavily weighted by USDA oversight to a more self-regulated format wherein the poultry producer shoulders more of the inspection burden. As a consequence, there has been additional heightened awareness and recognition of the need for greater product safety, including the reduction of microbial contamination levels.

The poultry industry has been actively seeking intervention methods designed to meet the current USDA regulations for continuous on-line processing. These regulations deal with the corrective actions that are mandated to remove carcasses that have been contaminated during evisceration with digestive tract materials. The regulations require that these contaminated carcasses be removed from the main processing line and transferred to an approved reprocessing line where the contamination can be removed by washing, trimming, vacuuming or a combination of these steps.

Prior method disinfection and processing goals have been to act as an intervention step which allows for the continuous on-line processing of poultry carcasses using a single point treatment which utilizes either trisodium phosphate washing or acidified chlorite. In general, single point treatment of a rapidly moving carcass on a production line is insufficient to meet the complex food safety requirements in a poultry processing plant. The single point treatment system using trisodium phosphate washing is described in U.S. Pat. No. 5,882,253. In the case of trisodium phosphate, the process is further disadvantaged by the introduction to the plant's operations of increased levels of nutrients such as phosphates (i.e;, a byproduct of trisodium phosphate) that may need to be removed in the plant's wastewater operations due to environmental discharge regulations or concerns.

Such environmental discharge regulations and concerns require that poultry processing plants decrease the level of nutrients such as phosphates in wastewater discharge. Additionally, the application of trisodium phosphate elevates the pH of the carcass being processed, as well as the process water all of which carries over to the plant's chill system. The increased pH level in the chill system makes downstream chlorine disinfection less effective without significant chemical additions.

As discussed above and as dictated by the state of the art poultry or carcass processing plants, the current processes fail to appreciate the benefits associated with pH control, multiple point controlled treatment, or even the unexpected advantages to be gained by reducing the organic loads within such process water. By failing to appreciate these requirements, the conventional approaches commonly suffer from difficult treatment challenges and as a result, these approaches have been accompanied by disadvantageously high operating costs and reduced efficiency. This has in turn translated in to reduced product quality and reduced processing plant productivity.

SUMMARY

The various objects and aspects of the present invention are met using an approach which focuses on appropriately regulating and controlling the pH of the process water to be disinfected and through addition, regulation and control of a disinfecting agent. The control of pH and level of disinfecting agent is implemented throughout multiple steps in the production process including any process water to be recovered and reused. This is in contrast to prior approaches which have failed to appreciate the benefits associated with pH control, multiple point controlled treatment, or even the unexpected advantages to be gained by reducing the organic loads within such process water.

Advantages of the present invention comprise processes which allow for the automated regulation of the pH of poultry processing water, preferably at certain stages of the process, so as to dramatically improve the efficiency and effectiveness of antimicrobial or other disinfection agents added. The poultry process treatment water which can especially benefit includes the water used in poultry scalding, picking, post-pick washing, evisceration, carcass washing and other stages of poultry processing designed to physically remove any fecal matter, ingesta and other digestive tract remnants from the slaughter and evisceration processes. Additionally, an improved device and method are provided for effecting economic and efficient regulation of disinfection agent and control of the disinfection chemistry throughout the multiple steps of the production process.

Physical removal of visible fecal material and other contaminants from poultry carcasses will be carried out by serial carcass washing steps (e.g., scalder, picker, post pick spray wash, inside/outside carcass washing cabinets and outside carcass washing cabinets) where medium pressure, high volume water spraying is employed. The introduction of USDA approved antimicrobial agents (e.g., calcium hypochlorite or others), applied at optimum pH control level

for chlorine disinfection at multiple treatment stages (e.g., scalder, picker, post pick spray wash, inside/outside carcass wash and outside carcass wash) and using the best practical control methods is designed to significantly reduce microbial levels on all carcasses prior to and after their entry into the submersion chiller system.

The invention described herein is designed to employ the advantages of controlled chlorination (e.g., calcium hypochlorite and/or other USDA approved food grade biocides) at optimum pH levels, together with the proven effectiveness of increased contact time (CT) through the implementation of multiple stage treatment of the carcass during slaughter, evisceration, washing and chilling.

Additionally, an improved device and method are provided for effecting economic and efficient regulation of disinfection agent effectiveness comprising a system and method for removing a major portion of filterable materials including fats, oils and greases (FOG), total suspended solids (TSS), proteins, blood products, lipids and other materials represented as total is chemical oxidation demand (COD) from the chiller tank water.

The presently disclosed disinfection process for use in the processing of foodstuffs is designed as an intervention step in poultry processing to allow for continuous on-line processing of poultry carcasses that may have accidentally become contaminated during the evisceration process. Such on-line processing is designed to replace the need for off-line manual washing and cleaning of the contaminated carcasses. By eliminating such off-line manual washing, food safety will be enhanced due to the elimination of the physical handling of carcasses and the cross-contamination that may result from such physical handling. An additional benefit is that it will be possible to run the production process with a reduced number of interruptions, which will result in a more efficient production process. The disinfection process according to the present invention, include: the removal, using the processing plant's existing washing, spraying and mechanical scrubbing devices (modified if required), of visible fecal material or other contaminants from the carcasses resulting from the mechanical evisceration process; the introduction of an enhanced antimicrobial treatment agent at multiple stages to improve food safety by reduction of total microbial levels; the improvement of disinfection in the facility's overall production process including the carcass chiller system through the use of pH controlled chlorination to further reduce microbial counts, and the reduction of the amount of physical handling of carcasses and therefore, reduction of the potential for cross-contamination.

Further, the present invention is specifically designed to be easily incorporated into the processor's existing production equipment and plant layout. This ease of implementation is accomplished by using, to the greatest extent possible, the processor's existing carcass wash stations, scalders, pickers and other designated treatment points as the point of treatment by using the existing water piping and delivery systems as the means of delivery of the invention's chemical and disinfection enhancements.

The invention described herein is designed to meet the current USDA regulations for removal of visible fecal material using the plant's existing washing, spraying and mechanical scrubbing devices, and to reduce microorganism counts and improve food safety, all in a more cost effective and environmentally friendly manner than other approaches.

An additional benefit of the invention relates to those poultry processors who have or who intend to implement water reuse programs. Such water reuse programs, as is the subject of U.S. application Ser. No. 09/507,163, filed Feb. 18, 2000 and which is hereby incorporated by reference in its entirety, have met with favorable and advantageous results by returning reuse water that has been disinfected with ozone and then chlorinated at an advantageous dosage before being reintroduced to the production process at an upstream point, such as in the scalder or similar heating portion of the processing steps. The reintroduction of the chlorinated reuse water into the scalder or similar heating processing step causes a dramatic reduction in the levels of microorganisms associated with the carcasses that have not been found in the prior art. Also, it is an embodiment of the present disclosure, to introduce chlorinated and/or ozonated water (or other approved disinfectant) along the foodstuffs processing steps, particularly along the points where the use of heated water is applicable, such as in the scalder or similar processing steps which subject the carcasses to heated water. In such heated processing steps, the pores and tissue membranes of the carcasses are open and are more readily receiving of the surrounding water, i.e., the chlorinated and/or ozonated water, thereby having greater efficacy to the removal of microorganisms associated with such foodstuff processing.

In view of the foregoing, the advantages of the present disclosure include providing new methods for improving the effectiveness of the disinfection agent being used, new methods for improving the decontamination of poultry or other foodstuff and the water used in the processing of said poultry and other foodstuff, and water reuse methods which cause a reduction in the levels of microorganisms associated with the carcasses.

BRIEF DESCRIPTION OF THE DRAWINGS

The objects and features of the present disclosure, which are believed to be novel, are set forth with particularity in the appended claims. The present disclosure, both as to its organization and manner of operation, together with further objectives and advantages, may best be understood by reference to the following description, taken in connection with the accompanying drawings, in which:

FIG. **1** depicts a flow chart of the multi-stage chlorination process and chiller treatment system according to the present disclosure;

FIG. **2**A provides a more detailed flow plan of the multi-stage chlorination process of FIG. **1**;

FIG. **2**B provides a more detailed flow plan of the chiller treatment system of FIG. **1**; and

FIG. **3** depicts an alternate view of the chiller treatment system according to the present disclosure.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

The preferred embodiments of the apparatus and methods disclosed herein are discussed in terms of a disinfection process designed as an intervention step in poultry processing to allow for continuous on-line processing of poultry carcasses that may have accidentally become contaminated during the evisceration process. It is envisioned, however, that the disclosure is applicable to a wide variety of processes including, but not limited to, general carcass or foodstuffs processing including processing operations used in poultry, beef and pork slaughter plants.

As discussed throughout the present disclosure, the control of the pH of the treatment water within product processing water optimizes the elimination of pathogens and

other microorganisms. Also, by providing an intervention step to allow for continuous on-line processing of poultry carcasses, there is a reduction in the amount of physical handling of carcasses and therefore, a reduction in the potential for cross-contamination of the carcasses, thereby improving quality and food safety. The present disclosure also discloses methods and devices for improving the effectiveness of disinfection agents in chiller tank processing water by substantial removal of filterable materials. A particular advantage is the fact that the methods of the present invention can be "retrofitted" to existing processing plants without any significant alteration of the plant's "footprint" or layout.

While the processes and devices described will be equally applicable to the aqueous processing of a variety of foodstuffs, for convenience, the application to the poultry processing industry will be described. This industry uses significant volumes of water in its processing operations. Much of the water used during such processing is regulated by the USDA, although the quantity and process steps vary from plant to plant. On average, the typical slaughter plant will use between 5 and 15 gallons per animal, divided into several key elements:

The Scalding process—USDA guidelines dictate a minimum of 1 quart per animal.

The Picking (de-feathering) process—varies from plant to plant.

The Evisceration process—varies from plant to plant.

Carcass washing (including Inside/Outside Carcass Washers, Intermediate Wash Stations and Final Rinse Cabinets)—these combined carcass wash steps can use between 2 and 6 gallons per animal.

The Chilling process (chillers)—USDA guidelines require minimum overflow rates of 0.5 gallons per animal in whole bird chiller tanks and temperature control. Various processors also utilize chilled water for "paws", gizzards and other edible organs sold commercially. Typical chiller operations can consume between 0.75 and 1.5 gallons per animal.

Plant Sanitation—plant sanitation can use between 1.5 and 3 gallons per animal.

Equipment wash—a typical processing plant will use between 0.25 and 1 gallon per animal in equipment washing (this is an "on-line" process and should be differentiated from sanitation during which the entire plant and equipment is washed and sanitized when the plant is not in production).

Miscellaneous water usage—truck wash, live loading shed wash, domestic water, wastewater and industrial (non-product contact uses such as evaporative cooling for refrigeration, vacuum pump seal and cooling and compressor cooling) wash.

Most of the water is used during the evisceration and carcass washing steps and is typically applied by mechanical mechanisms comprising spray washing devices, cabinet type washers, brush washers and medium and/or high-pressure water spraying heads. The present invention takes advantage of the use of these existing water processing steps and mechanisms in improving the disinfection of the processing water and thus the processed foodstuff thereby improving its quality and safety.

Referring to FIGS. **1**, **2**A and **2**B, the physical aspects of the present disclosure are illustrated as a common header **12** (either existing in the processing plant or, modification of the plant's water delivery system or, a custom, site built common header) used as the delivery mechanism to convey the treated water (e.g., calcium hypochlorite plus pH control) to the designated treatment points in the process. A tablet or liquid chlorine feed system **14** sized to deliver the maximum practical and allowable dosage of chlorine to the entire volume of water required to serve the multiple stages of treatment is situated along the common header **12**. Also situated is a gas/liquid or, liquid/liquid injection device **16** to permit the introduction of the preferred acidification agent (e.g., CO_2, or other chemical agent) into the water in the delivery header to alter the levels of pH in the treatment water based on the readings of the pH probe **18**. A control panel **20** is used along the process in order to monitor the readings and control the dosages of the chemical agents required to perform the disinfection and pH control **22**. Multiple sensors **24** are located along the common header **12** in order to monitor, control the conveyance of the enhanced disinfection chemistry, measure chlorine levels and pH levels and send via electronic signal (feedback loops) the measurements to the proper chemical controllers.

The present disclosure makes use of (with or, without modifications) the plant's existing carcass wash cabinets and mechanical washing devices **26** to assist in the removal of visible contamination and serve as treatment points for the delivery of the enhanced disinfection chemistry. Devices for scalding, feather picking, post-pick washing and evisceration line washing stations act as additional treatment points for the delivery of the enhanced disinfection chemistry, as well as the plant's water recycle and reuse system **28**, where the water has been disinfected with ozone (ozonated) or other appropriate disinfectant and then dosed with an appropriate level of an approved disinfection agent (e.g., calcium hypochlorite or others) before being reintroduced into the production process at an upstream point, such as in the scalder or similar heating portion of the processing steps. An alternative to the disclosed water recovery and reuse system **28** is an ozonating or chlorinating system **29** which simply ozonates or chlorinates outside water and reintroduces such water to any or all of the heated processing steps, i.e. the scalder step, the picker step and the post-pick step, which utilize heated water (heated water being defined as water used during poultry processing which is or was heated at some point, preferably, but not limited to, at the scalder step). This reintroduction, like with the water recovery and reuse system **28**, reduces the levels of contamination within the poultry.

Multi-Stage, Controlled pH Chlorination During Poultry Processing

While the USDA mandates the use of a disinfection agent (typically chlorine) at various stages of the poultry processing operations, it is silent concerning the conditions under which the as disinfection agent is employed. It has been discovered that the effectiveness of the disinfection agent may be dramatically altered by characteristics of the processing water being treated, most notably pH, but also by the solute load presented by filterable materials. Other aspects of the present invention lie in the ability to improve the disinfection quality of the processing water at multiple points during processing. This becomes important because the effectiveness of a disinfection agent is directly proportional to the time in which the microorganisms to be killed are in contact therewith. The importance of contact time has been reflected in the US Environmental Protection Agency's (USEPA) Contact Time "CT" Values, in its guidelines concerning the disinfection of drinking water. These relationships have been perhaps most clearly spelled out by a mathematical formula developed by Chick in 1908, which described the kinetics of disinfection:

$$N_t = N_0 \exp(-kt)$$

Where:

N_t=number of microorganisms surviving after time t

N_0=initial number of microorganisms

−k=rate constant dependent upon type of microorganism and disinfectant

t=time the organisms is in contact with the disinfectant

USEPA CT Values are expressed as mg/L-min; where

mg/L=concentration of disinfectant

min=time in contact with disinfectant

Clearly then, the longer and/or more often that the microorganisms (whether in the water or on the poultry being processed) come into contact with the disinfectant, the greater the reduction of microorganisms and the safer the poultry.

However, it has been discovered that there are still other factors which must be considered, including those which affect the efficacy of the disinfection agent. Several of the embodiments of the present invention take advantage of methods of optimizing these factors, chief amongst which is pH. The temperature and pH level of the water into which the disinfection agent, e.g. chlorine, is introduced can dramatically affect the effectiveness of the disinfection agent. This is illustrated by Tables 1–7 shown below, which are published by the USEPA concerning guidelines to CT values (lower numbers mean higher antimicrobial efficacy) in drinking water. These tables show the dramatic improvement in effectiveness of chlorine and chlorine derivatives at both lower pH and higher temperature. The tables also demonstrate how different microorganisms react differently to disinfection agents, e.g., viruses require longer contact periods to be inactivated.

The methods of the present invention capitalize upon these effects by adjusting the pH of the processing water to levels between pH 5 and 8, most preferably between pH 6.5 and 7, and by bringing such pH controlled disinfecting water into contact with the carcasses at multiple processing points. While the level of hypochlorous acid will continue to increase as pH levels continue to decline (thereby resulting in greater anti-microbial activity), the resulting corrosive nature of liquids with severely depressed pH can have deleterious effects upon plant equipment, not to mention hazard to equipment operators and hence, such reduced pH levels do not represent the optimum practical levels. The inverse of this is also true.

TABLE 1

CT Values for 3-log (99.9%) Inactivation of Giardia Cysts By Free Chlorine at Water Temperature 10.0° C. (50° F.)

Free Residual	pH						
mg/L	≦6.0	6.5	7.0	7.5	8.0	8.5	≦9.0
≦0.4	73	88	104	125	149	177	209
0.6	75	90	107	128	153	183	218
0.8	78	92	110	131	158	189	226
1.0	79	94	112	134	162	195	234
1.2	80	95	114	137	168	200	240
1.4	82	98	116	140	170	206	247
1.6	83	99	119	144	174	211	253
1.8	88	101	122	147	179	215	259
2.0	87	104	124	150	182	221	265
2.2	89	105	127	153	186	225	271
2.4	90	107	129	157	190	230	276
2.6	92	110	131	160	194	234	281
2.8	93	111	134	163	197	239	287
3.0	95	113	137	166	201	243	292

TABLE 2

CT Values for Inactivation of Viruses By Free Chlorine

Temperature, ° C.	Log Inactivation 2.0-log pH 6–9	2.0-log pH 10	3.0-log pH 6–9	3.0-log pH 10	4.0-log pH 6–9	4.0-log pH 10
0.5	6	45	9	66	12	90
5	4	30	6	44	8	60
10	3	22	4	33	6	45
15	2	15	3	22	4	30
20	1	11	2	16	3	22
25	1	7	1	11	2	15

Note: CT values can be adjusted to other temperatures by doubling the CT for each 10° C. drop in temperature.

TABLE 3

CT Values for Inactivation of Giardia Cysts By Chloramine Within the pH Range 6 to 9

Inactivation	Temperature, ° C. ≦1	5	10	15	20	25
0.5–log	635	365	310	250	185	125
1–log	1270	735	615	500	370	250
1.5–log	1900	1100	930	750	550	375
2–log	2535	1470	1230	1000	735	500
2.5–log	3170	1830	1540	1250	915	625
3–log	3800	2200	1850	1500	1100	750

TABLE 4

CT Values for Inactivation of Viruses By Chloramine*

Inactivation	Temperature, ° C. ≦1	5	10	15	20	25
2-log	1243	857	643	428	321	214
3-log	2063	1423	1067	712	534	356
4-log	2883	1988	1491	994	746	497

*This table applies for systems using combined chlorine where chlorine is added prior to ammonia in the treatment sequence.

TABLE 5

CT Values for Inactivation of Giardia Cysts By Chlorine Dioxide Within the pH Range 6 to 9

Inactivation	Temperature, ° C. ≦1	5	10	15	20	25
0.5-log	10	4.3	4.0	3.2	2.5	2.0
1-log	21	8.7	7.7	6.3	5.0	3.7
1.5-log	32	13.0	12.0	10.0	7.5	5.5
2-log	42	17.0	15.0	13.0	10.0	7.3
2.5-log	52	22.0	19.0	16.0	13.0	9.0
3-log	63	26.0	23.0	19.0	15.0	11.0

TABLE 6

CT Values for Inactivation of Giardia Cysts By Chloride Dioxide Within the pH Range 6 to 9

Inactivation	Temperature, ° C. ≦1	5	10	15	20	25
0.5-log	10	4.3	4.0	3.2	2.5	2.0
1-log	21	8.7	7.7	6.3	5.0	3.7
1.5-log	32	13.0	12.0	10.0	7.5	5.5
2-log	42	17.0	15.0	13.0	10.0	7.3

TABLE 6-continued

CT Values for Inactivation of Giardia Cysts By Chloride Dioxide Within the pH Range 6 to 9

Inactivation	Temperature, ° C. ≦1	5	10	15	20	25
2.5-log	52	22.0	19.0	16.0	13.0	9.0
3-log	63	26.0	23.0	19.0	15.0	11.0

TABLE 7

CT Values for Inactivation of Viruses by Chorine Dioxide Within the pH Range 6 to 9

Inactivation	Temperature, ° C. ≦1	5	10	15	20	25
2-log	8.4	5.6	4.2	2.8	2.1	1.4
3-log	25.6	17.1	12.8	8.6	6.4	4.3
4-log	50.1	33.4	25.1	16.7	12.5	8.4

Accordingly, the preferred methods of the present invention incorporate the introduction of chlorine, a chlorine derivative (a preferred disinfectant agent), ozone or other approved disinfectant at a controlled pH (adjusted appropriately for the disinfectant employed given the additional practical considerations previously described). The introduction of such disinfectant in a combined system of chlorine injection (or mixing) and acidification (using carbon dioxide, citric acid, lactic acid or any other acid compound (s) approved for contact with food products by the USDA) into solution of the feed water is used in the following processing stages: the Scalders, the Pickers, the Post pick washers, the Inside Carcass Washers, the Inside/Outside Carcass Washers, the Outside Carcass Washers, the Final Carcass Washers and any other practical stage where water is used to physically remove contamination.

Similarly, disinfection of the foodstuffs are realized from the production of "chloramines" during the "up stream" introduction of the treated reuse water into processes employing elevated water temperatures. According to the present disclosure, the water reuse system incorporated in a poultry processing plant does not remove significant levels of nitrogen or ammonia from the process water which, subsequent to the ozonating step, combines with added chlorine passing through the cascade process, i.e., the gathering of process water from a number of source points in the production line, thereby forming various "chloramines" which, in the environment of elevated temperatures, aides in the reduction of microorganisms in the foodstuffs.

The processes of the present invention take advantage of frequent surface and internal contact of the disinfectant with the carcass to increase microorganism lethality and the disinfectant remaining on the carcass external surface and internal surfaces to allow for additional time between the various process stages. Therefore, by beginning the treatment or disinfection process at earlier stages of poultry carcass processing, many advantages are realized.

First, introducing disinfectant at earlier stages results in inactivation (kill) of additional potentially pathogenic organisms not addressed in the current practices. The carcass will be at a higher temperature directly after the scalder stage and into the "post pick" stage. Higher carcass temperatures result in opening of the pores on the carcass skin and loosening of the skin from the muscle tissue. At these conditions, the disinfectant will contact surfaces and tissues that later become unavailable (e.g. closed) as the carcass temperature falls (especially in the chiller tanks).

Second, introduction of disinfectant during evisceration, the disinfectant will contact the surfaces of the carcass at the stage when potential contamination with fecal material or ingesta is most likely. Additionally, some residual disinfectant will be carried over to the next stage allowing for additional contact time.

Third, carcass washing with water treated with disinfectant, whether carried out in one stage or in multiple stages (various processors utilize different methods, washer designs and frequency of washers), will again allow for additional surface contact with the disinfectant at its highest efficiency (due to controlled pH).

Lastly, the entire process at these stages is also designed to reduce the contaminant (microorganism) load as the carcass is sent to the chillers. Any reduction in the organic loading prior to the carcass entry into the chiller tank will serve to reduce the risk of cross-contamination when the carcasses are immersed in a common tank (communal bath).

The following chart reflects an example of time "t" value potentials using Multi-Stage Chlorination (at controlled pH) during poultry processing:

Stage	Direct Contact Time	Time Between Stages	Cumulative Time "t"
1. Scalders	60–120 seconds	5–20 seconds	65–140 seconds
2. Pickers	30–90 seconds	6–9 seconds	36–99 seconds
3. Post Pick Wash	5–15 seconds	5–10 seconds	10–25 seconds
4. IOBW Wash	10–30 seconds	6–16 seconds	16–46 seconds
5. Final wash	10–30 seconds	8–18 seconds	18–48 seconds
Total Time			2.4–6.0 minutes

Enhanced Disinfection of Carcasses in Poultry Chiller Tanks

In an alternative embodiment, there is incorporated some of the same disinfection enhancements, as previously described, i.e., introduction of the disinfectant at pH levels where the maximum "active" compound is present in the poultry chiller tanks. Current practices and USDA guidelines require chiller tanks to be monitored for chlorine residual or total chlorine. The concentrations and testing protocols required vary from plant to plant. Generally because there are no specific mandates for disinfection of chiller tanks, there tends to be no uniformity in approach. The processes of the present invention benefit from utilization of an equipment package designed to continuously monitor and adjust the introduction of acidification to control pH level in the chiller tank as to allow for the maximum potential effective formation of hypochlorous acid (in those circumstances where chlorine is used) to enhance the disinfection process.

Similar practical considerations apply with respect to heat and the disinfection process. The invention is advantageously designed to utilize the elevation in water temperature at the scalding stage of the slaughter process. In poultry scalders, as well as the poultry picker and post-pick steps, the temperature of the water (and hence the poultry contained therein) is elevated to between 140 degrees F. and 170 degrees F. At these temperatures, the animal's skin releases from the muscle tissue and allows the aqueous chlorination to contact a larger surface area of the carcass. Also, the elevated temperature results in a higher reaction rate of chlorine reaction. Accordingly, the methods of the present invention, which provide controlled dosing of a disinfection

agent, ideally will apply beginning with those processing steps which follow the initial slaughter steps.

With reference to FIGS. **2**A and **2**B, an advantage of the present invention includes the employment of a chiller tank water quality enhancement process. This process is ideally designed to continuously remove "filterable materials" from the chiller tank including FOG, TSS and COD. Disinfection is commonly affected by an oxidation process where the oxidant (e.g., hypochlorous acid, hypobromous acid, chlorine dioxide, ozone, hydrogen peroxide etc.) is the active disinfection agent. Since the oxidative reaction by the oxidation agent in water is a non-preferential one, the presence of high organic loading will pose a correspondingly higher oxidant demand to achieve comparable inactivation of microorganisms. To improve efficiency, the present inventive methods remove organics such as FOG, TSS and COD from the water to permit use of a lower disinfectant dosage to achieve the desired disinfection standard or "kill efficiency."

These methods can ideally be practiced with the preferred devices of the present invention which comprise mechanism (s) for continuous "mass load" organic removal. This is ideally accomplished by the use of mass removal by floatation, screening or other suitable means, followed by fine filtration using Diatomaceous Earth (DE) filters, membranes or other suitable methods of removing the identified "filterable" materials. It has been discovered that this will enhance the chiller tank's water quality, reduce significantly the disinfectant demand and greatly increase the efficiency of employing disinfection at this critical stage of the process.

The ideal process utilizes an equipment package designed to continuously monitor and adjust the introduction of acidification to control pH in the chiller tanks, and allows for the maximum potential effective formation of hypochlorous acid (where chlorine is used) to enhance the disinfection process. As previously described, the chiller water treatment equipment consists of similar equipment packages.

Using the USEPA CT values, this stage represents the highest potential for disinfection enhancement. This is due to the length of time the carcass is immersed in the chiller bath (typically between 1.5 and 3.0 hours). Assuming a disinfectant dosage that will result in 5.0 ppm "free residual", the resulting CT credit equates to 450–900 mg/L-min.

While the description of the present invention focuses on the use of some form of chlorine as the disinfection agent, it is important to note that other disinfection agents may be advantageously applied at one or more steps in the process. Disinfection agents such as chlorine dioxide, ozone, chlorites, etc., may be used to increase the effectiveness of the process.

In addition, the methods for improving disinfection processes may be advantageously combined with improved methods of water recovery and re-use within the processing plant (see, for example, U.S. application Ser. No. 09/507,163, filed Feb. 18, 2000, and previously made part of this disclosure by incorporation). Under such an approach, process water will be taken from the processing operations, filtered and disinfected to levels determined by the USDA. In such a system and following filtration, the filtered water is pumped by a centrifugal, end suction, top discharge pump to a disinfection system. Disinfection of the water is accomplished by the introduction of gaseous ozone into the filtered water. Ozone is generated by a corona discharge type ozone machine using cryogenic oxygen or, oxygen separated by pressure swing adsorption on-site as the parent gas. The ozone is preferably introduced into the filtered water by way of a venturi type gas/liquid mixing device (Mazzei Injector). The ozonated water is pumped through a pressure dwell manifold or a high efficiency, centrifugal gas/liquid-mixing device to promote maximum dissolution of the ozone gas. The ozonated water flows to an ozone contact tank (304 stainless steel) ideally sized to achieve a minimum of about 7 to 10 minutes of contact time. Ozone generator sizing is based on USEPA criteria for 3 to 4-log removal efficiency at an applied dose of a maximum of 7 ppm and a standard of 5 ppm. The ozone contact tank is fitted with either a dissolved ozone measuring device or an Oxidation-Reduction Potential (ORP) probe. This probe is interfaced with the dissolved ozone monitor or the ORP monitor in the system's main control panel, and dissolved ozone level or ORP is constantly displayed on the panel front. ORP and/or dissolved ozone is ideally controlled to achieve the desired disinfection standard determined by microbiological analysis at various dissolved ozone or ORP set points to assure that the water is pathogen free. A 750-mv set point is commonly used to indicate the sterility of water. The International Bottled Water Association (IBWA) and others indicate that, at this level of oxidation, the water is deemed sterile by drinking water standards and that microbiological activity is eliminated. An alarm is activated if ORP falls below the programmed setpoint and the system can be shut down. Following disinfection by ozonation, the water is rechlorinated at an advantageous dosage before being returned to the scalder or other heating processing steps.

As can be seen from FIGS. **1** and **2**B, the apparatus for employing the embodiments of the enhanced disinfection of carcasses in poultry chiller tanks **30** includes the following primary components: the disinfectant distribution system **32**, pH control system **34** including acid control **40**, on-line monitoring **36**, organic mass removal system **38** (filtration for chiller tanks), a water reuse system **28**, and/or an ozonating or chlorinating system **29**.

The disinfectant distribution system **32** is designed to introduce, through direct injection into the process stream, the desired disinfectant. This sub-component may be advantageously configured for liquid/liquid injection and mixing, gas/liquid injection and/or solid dissolution followed by liquid/liquid injection. There are several common forms of disinfectant currently employed by the processing industry, including sodium hypochlorite, calcium hypochlorite, chlorine dioxide, ozone and others. It will be readily appreciated by those skilled in the art that each of these disinfectants will require a slightly different means of introduction into the process water stream.

The pH control system **34** is dependent upon the level of pH and the disinfectant employed. For sodium hypochlorite and calcium hypochlorite, the pH control system will preferably involve the introduction of acidification compound at a controlled and monitored rate. The rate of introduction (whether liquid/liquid or gas/liquid) will be monitored and proportionally controlled by the use of a PID or PLC type device to ensure that the pH level is controlled within a tight control band (i.e., for chlorine compounds 6.5–7.0 pH). On line monitoring allows for continuous monitoring of the treatment water by the use of pH probes **36** installed in the piping and distribution system. This assures that the pH level is at the desired "optimum" for the disinfectant employed.

An organic mass removal system **38** (filtration for chiller tanks) incorporates one or more steps designed to remove by physical separation, the organic contamination being constantly introduced to the carcass chiller tank(s) **30**. Each animal carcass will have some materials that have not been removed in prior washing. These materials include soluble

and insoluble fats, oils, skin, blood products and other contaminants as previously described. The filtration system **38** is designed to remove either all or a major portion of these "filterable solids" in order to reduce the oxidant demand in the chiller tank **30** and thus permit reaching a higher disinfection standard.

As an essential step in the poultry processing system, the chilling process includes vessels into which the poultry carcasses are introduced from the plant's processing lines to reduce temperature of the meat, control bacterial growth through chemical disinfection and hydrate the carcass within the USDA limits of acceptable water content. The process described herein is directed at maintaining the best conditions for chemical disinfection in poultry chiller tanks. As background for such processes, the U.S. poultry industry employs immersion chilling for poultry, carcasses through the use of large volume, stainless steel tanks where the product is mechanically introduced from the processing line(s) after evisceration and inspection.

With reference to FIGS. **2**B and **3**, such poultry chillers **30** are connected to refrigeration loops, referred to in the industry as a "red water chiller(s)," for the purpose of rejecting heat from chilled water systems. Typically, these red water chiller recirculating systems **42** are closed loop heat exchangers operating with ammonia gas as the refrigerant and electric drive motors to provide the compression/expansion or state change of the refrigerant. The refrigeration chiller **42** typically operates as a closed recirculating loop, where the chiller acts as the heat exchanger to remove heat from the system water in order to maintain the USDA mandated temperature in the chiller tanks.

A mass removal system **38** is designed to continuously remove organic and solids content from the plant's chiller tanks **30** using screening, floatation, filtration and oxidation. The carcasses entering the chiller tanks **30** bring "contaminants" which may be of an organic or inorganic nature and consist of fats, oils, grease, blood products, proteins, lipids and pieces of skin and organs that may have remained after the evisceration. Other inorganic contaminants typically consist of minerals dissolved into the water such as phosphates, nitrogen compounds and other constituents originating in the animal feed or the water used in washing and chilling. The chiller tanks **30** are filled before the first processing shift and are constantly refreshed with potable water during the plant's processing hours (the USDA maintains a requirement of one-half (½) gallon of makeup water per bird). The entering makeup water replaces a similar volume of chiller tank overflow being dispensed from the tank **30**. This enables a refreshing of the chiller tank **30** to counteract the cumulative effects of concentration of the contamination brought into the tanks **30** with the carcasses.

It is known that the cumulative effects of constant introduction of the contaminants does negatively impact the effectiveness of carcass disinfection and microbial control. When analyzed for contaminant content, the water from chiller tanks **30** shows that there is a significant level of organic compounds that compete chemically with the microbial content for oxidizer demand. As such, most processing plants have had difficulties in controlling chlorine levels due to the presence of high organic loading.

The carcasses will typically remain in the chiller tanks **30** for between **45** minutes and several hours. The dwell time will be determined by the carcass weight, number of carcasses and efficiency of the chiller system in terms of refrigeration capacity. The controlling factor is the time required to achieve the temperature set by the USDA. The relatively long dwell times should provide an excellent opportunity for microbial control based on the previously described principals of contact time (CT). The limiting factor, however, is overcoming the organic loading resulting from the constant contaminant influx.

As discussed earlier, the process developed according to the present disclosure is directed at providing a continuous, on-line contaminant removal mechanism. The process is effected by the installation of mechanical separation, floatation and filtration devices **38** which are designed to remove organic compounds from the chiller tanks **30**. This mass removal of the organic compounds is accompanied by the implementation of enhanced disinfection/microbial control using the most favorable chemistry for chlorination **32**, **34**, **40**. The chemistry, as previously described herein, consists of the combination of pH control **34** and chlorine or other disinfectant injection **32**.

The continuous separation, floatation, filtration mechanism **38** for mass removal of the contaminants being introduced into the chilled water tanks **30** is connected to the chiller tank **30** by way of interconnecting piping where a constant volume of water is pumped from the chiller tanks **30**, sent to the contaminant removal apparatus, cleansed and returned to the chiller tanks **30**. The process is designed to operate continuously. Maintenance of chiller tank water quality is dictated by the disinfection efficiency as measured by the chlorine monitoring devices.

With particular reference to FIG. **3**, the chiller tank treatment system process is designed to allow for maximum flexibility of operations based upon the site-specific conditions, load profile and economics. The observed range of chiller system water quality varies significantly across the spectrum of poultry processing plants. In some cases, the operation of the chiller system, together with the size, weight and process rate of birds, will allow a solution that may not require the same mass removal of contaminants as others. A time weighted load factor should be analyzed to assist with the sizing and specification of the components and overall system configuration. This procedure can be accomplished by taking numerous samples of the bulk water in the chiller tanks **30** over a specified period of time. A plot of the contaminant loading will yield a load per hour rate or a load per carcass rate that is important to the sizing and configuration of the treatment solution. A target water quality is established based on the disinfection chemistry and a treatment system is sized to remove the required mass load of contaminants to consistently maintain the target water quality.

The first stage of the system involves pumping water from the chiller tanks **30**, by way of a dedicated pump **70** to the treatment system's first stage unit operations. This stage includes a mechanical screening device **72** such as a double drum rotating type, where the influent water is introduced into the internal portion of the device. The double drum screen includes a larger mesh screen as its internal first stage, and a smaller mesh as its external second stage. As the solids are captured on either the internal or external screen surfaces, a traveling, high-pressure water spray nozzle, directed at the surface of the screen, forcibly removes the trapped solids and enhance the screen's ability to maintain flow capacities. The screened water is captured by gravity in a sump located below the screens. The sump is fitted with level sensors to interface with a pump fitted to the sump to allow for automatic operation and to prevent the pump from "dry cycling" when no water is available to pump.

The screened water, now having the preponderance of large solids removed, is pumped to the system's floatation unit **74**. This floatation unit **74** could be either of the induced

or dissolved air type. Selection of the best method is based on site-specific load characteristics and the targeted mass removal efficiency. Air floatation is well-documented in the literature and operates on well-understood principles of vertical bubble velocity and the ability to attract solids and colloidal materials. Simple skimming and/or overflow removes the floated material. Typical floatation devices are easily adaptable to accept chemical assistance in the form of coagulants, flocculants and other treatment chemicals designed to enhance removal efficiencies. The use of any such chemical assistance would be subject to FDA and USDA regulations and guidelines relating to food quality and safety.

The now screened and floatation treated water is then flowed to the filtration device **76** which removes smaller solids. The selection of the filtration device **76**, such as a media filter, will depend upon site-specific conditions. The media filter can use diatomaceous earth as its media and the filter vessel could be of a vacuum leaf, rotating vacuum drum, or pressure leaf design. The smaller solids not removed by the previous stages (screening and floatation) are trapped on the media filter's media matrix which, in the case of diatomaceous earth, has removal efficiencies capable of treating to small micron size particles. The effluent quality from such devices is quite high and is typically below 5 NTU's in turbidity. The treated water is now ready to be transferred back to the chiller tanks **30**. At any point along the above identified filtration steps **38**, the treated water can be monitored for turbidity via a monitoring device which allows the operator to monitor the system performance. Such a monitoring device can be installed anywhere in-line with alarms, feedback loops or recording devices, which enables total system performance and provides a base for implementing modifications.

It will be readily understood by those skilled in the art that various modifications may be made to the embodiments disclosed herein. Therefore, the above description should not be so construed as limiting, but merely as exemplifications of preferred embodiments. Those skilled in the art will envision other modifications within the scope and spirit of the claims appended hereto.

What is claimed is:

1. A method for improving the effectiveness of a disinfection agent added to an aqueous medium used in the processing of foodstuffs comprising the steps of:

controlling the pH level of the aqueous medium to a desired range of 6.0 to 8.0 through acidification prior to or concurrent with the addition of the disinfection agent to the aqueous medium.

2. The method for improving the effectiveness of a disinfection agent added to an aqueous medium according to claim **1**, wherein said step of adjusting further comprises acidification until the pH level of the aqueous medium is in the range of 6.5 and 7.

3. The method for improving the effectiveness of a disinfection agent added to an aqueous medium according to claim **1**, wherein said foodstuffs is poultry and said disinfection agent is chlorine.

4. In a method for processing poultry comprising the steps of scalding, picking, eviscerating, washing, rinsing and chilling said poultry using an aqueous medium, the improvement comprising the steps of:

controlling the pH level of the aqueous medium to a range of 6 and 8 through acidification prior to or concurrent with the addition of the disinfection agent to the aqueous medium;

recovering at least a portion of the aqueous medium from the chilling step;

filtering said recovered aqueous medium to remove particulate matter; and

reusing said filtered recovered aqueous medium in the chilling step.

5. A method for reducing the level of poultry contamination resulting from the processing of poultry, wherein the processing includes the steps of scalding, picking, eviscerating, washing and rinsing said poultry, the method for reducing the level of poultry contamination comprising the steps of:

adding a disinfectant to process water used in said processing steps;

controlling the pH level of said disinfected process water to a range of 6 and 8; and

using said disinfected process water at each of said processing steps, thereby reducing the level of contamination of the poultry at each of said processing steps.

6. The method for reducing the level of poultry contamination resulting from the processing of poultry according to claim **5**, wherein said step of adding a disinfectant to process water is performed prior to any of said processing steps.

7. The method for reducing the level of poultry contamination resulting from the processing of poultry according to claim **5**, wherein said disinfectant is selected from the group of chlorine, chloramine, chlorite, chlorine dioxide and ozone.

8. The method for reducing the level of poultry contamination resulting from the processing of poultry according to claim **5**, further comprising a step of monitoring and regulating said steps of adding a disinfectant to process water and said step of adjusting the pH level of said disinfected process water.

9. The method for reducing the level of poultry contamination resulting from the processing of poultry according to claim **5**, wherein the pH level of said disinfected process water is in the range of 6 and 8.

10. A method for reducing the level of poultry contamination resulting from the processing of poultry, wherein the processing of said poultry includes the steps of scalder, picker, post-pick, washer, rinsing and chilling, the method comprising the steps of:

recovering water used during at least one of said poultry processing steps;

treating said recovered water with a disinfectant and controlling the pH of said recovered water to a range between 6 and 8 to reduce microorganisms therein; and

reintroducing said treated water into at least one heated processing step which uses heated water, whereby the combination of said treated water and said heated water reduces the level of microorganisms within said poultry.

11. The method for reducing the level of poultry contamination according to claim **10**, wherein said at least one heated processing step is selected from the group of the scalder step, the picker step and the post-pick step.

12. The method for reducing the level of poultry contamination according to claim **10**, wherein said disinfectant is selected from the group of chlorine and ozone.

13. The method for reducing the level of poultry contamination according to claim **10**, wherein said step of treating said recovered water with a disinfectant includes ozonating and chlorinating said recovered water.

14. The method for reducing the level of poultry contamination according to claim **10**, wherein said disinfectant is selected from the group of chlorine, chloramine, chlorite, chlorine dioxide and ozone.

15. A system for reducing the level of poultry contamination resulting from poultry processing including the steps of scalder, picker, post-pick, washer, rinsing and chilling, the system including a water reuse and disinfection method, the water reuse method comprising the steps of:

recovering water used during at least one of said poultry processing steps;

treating said recovered water with a disinfectant to reduce the level of microorganisms therein; and

reintroducing said treated water into at least one of said poultry processing steps which uses heated water;

the disinfection method comprising the steps of:

adding a disinfectant to water used in said poultry processing steps;

controlling the pH level of said disinfected water to a range between 6 and 8; and

using said disinfected water in said at least one of said poultry processing steps which uses heated water, whereby the combination of said reuse water, said heated water and said disinfected water in said poultry processing steps reduces the level of microorganisms within said poultry.

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Applicant(s)

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Laura DiLorenzo--65755

If Required, Foreign Filing License Granted: 03/21/2011
The country code and number of your priority application, to be used for filing abroad under the Paris Convention, is **US 61/427,965**
Projected Publication Date: None, application is not eligible for pre-grant publication
Non-Publication Request: No
Early Publication Request: No
Title

IN SITU GENERATION OF PEROXYCARBOXYLIC ACIDS AT ALKALINE pH, AND METHODS OF USE THEREOF

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EXHIBIT G

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PTO/SB/16 (12-08)
Approved for use through 09/30/2010. OMB 0651-0032
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE

PROVISIONAL APPLICATION FOR PATENT COVER SHEET – Page 1 of 2

This is a request for filing a PROVISIONAL APPLICATION FOR PATENT under 37 CFR 1.53(c).

Express Mail Label No. FILED EFS-WEB

INVENTOR(S)		
Given Name (first and middle [if any])	Family Name or Surname	Residence (City and either State or Foreign Country)
Junzhong	Li	Apple Valley, MN
David D.	McSherry	St. Paul, MN
Richard K.	Staub	Lakeville, MN

Additional inventors are being named on the _____ separately numbered sheets attached hereto.

TITLE OF THE INVENTION (500 characters max):

IN SITU GENERATION OF PEROXYCARBOXYLIC ACIDS AT ALKALINE pH, AND METHODS OF USE THEREOF

Direct all correspondence to: **CORRESPONDENCE ADDRESS**

☒ The address corresponding to Customer Number: 43896

OR

☐ Firm or Individual Name

Address

City	State	Zip
Country	Telephone	Email

ENCLOSED APPLICATION PARTS *(check all that apply)*

☒ Application Data Sheet. See 37 CFR 1.76

☐ CD(s), Number of CDs _____

☐ Drawing(s) *Number of Sheets* _____

☐ Other (specify) _____

☒ Specification (e.g. description of the invention) *Number of Pages* 56

Fees Due: Filing Fee of $220 ($110 for small entity). If the specification and drawings exceed 100 sheets of paper, an application size fee is also due, which is $270 ($135 for small entity) for each additional 50 sheets or fraction thereof. See 35 U.S.C. 41(a)(1)(G) and 37 CFR 1.16(s).

METHOD OF PAYMENT OF THE FILING FEE AND APPLICATION SIZE FEE FOR THIS PROVISIONAL APPLICATION FOR PATENT

☐ Applicant claims small entity status. See 37 CFR 1.27.

☐ A check or money order made payable to the *Director of the United States Patent and Trademark Office* is enclosed to cover the filing fee and application size fee (if applicable).

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220

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The invention was made by an agency of the United States Government or under a contract with an agency of the United States Government.

☒ No.

☐ Yes, the name of the U.S. Government agency and the Government contract number are: _____

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SIGNATURE /Laura C. DiLorenzo/ Date December 29, 2010

TYPED or PRINTED NAME LAURA C. DILORENZO REGISTRATION NO. 65,755 *(if appropriate)*

TELEPHONE (651) 795-5490 Docket Number: _____

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IN SITU GENERATION OF PEROXYCARBOXYLIC ACIDS AT ALKALINE pH, AND METHODS OF USE THEREOF

CROSS REFERENCE TO RELATED APPLICATIONS

This application is related to U.S. Patent Application Serial No. _____(Attorney Docket No. 2839USP1), entitled Sugar Ester Peracid On-Site Generator and Formulator, filed concurrently herewith. The entire contents of this patent application are hereby expressly incorporated herein by reference including, without limitation, the specification, claims and abstract, as well as any figures, tables or drawings thereof.

FIELD OF THE INVENTION

The present disclosure relates to methods for the in situ generation of peroxycarboxylic acid compositions, at alkaline pH levels, viz. greater than about pH 12. The present disclosure also relates to methods for the in situ generation of mixed percarboxylic acid compositions, and methods of using the in situ generated peroxycarboxylic acid compositions.

BACKGROUND

Peroxycarboxylic acids are known for use as antimicrobials and bleaching agents. However, the most commonly used peroxycarboxylic acid, peroxyacetic acid, is known to have a strong pungent odor. Mixed peroxycarboxylic acid systems are also known for use as antimicrobial and bleaching agents.

Conventional peroxycarboxylic acid compositions are made through an acid catalyzed equilibrium reaction. Most often, the peroxycarboxylic acids are generated in a chemical plant, and then shipped to customers for on-site use. Due to the limited storage stability of peroxycarboxylic acids, the peroxycarboxylic acids must be packed in special containers and shipped under strict Department of Transportation (DOT) guidelines. Further, excess amounts of reagents (e.g., acids, oxidizing agents, and stabilizers) are present in the compositions during shipping to prevent decomposition.

SUMMARY

In some aspects, the present disclosure relates to peroxycarboxylic acid forming compositions. The compositions comprise an ester of a polyhydric alcohol and a C1 to C18 carboxylic acid, a source of alkalinity, and an oxidizing agent. The compositions are not at equilibrium, and have a pH greater than about 12. Further, the compositions are substantially free of a stabilizing agent, and a surfactant.

In other aspects, the present disclosure relates to mixed peroxycarboxylic acid forming compositions. The compositions comprise about 0.01 wt% to about 95wt% of a first ester of a polyhydric alcohol and a C1 to C18 carboxylic acid, about 0.01 wt% to about 95wt% of a second ester of a polyhydric alcohol and a C1 to C18 carboxylic acid, about 0.001 wt% to about 25 wt% of a source of alkalinity, and about 0.001 wt% to about 50 wt% of an oxidizing agent. In some embodiments, the first and second esters are not the same, the composition is not at equilibrium, and the composition is substantially free of a stabilizing agent.

In other aspects, the present disclosure relates to methods for forming a disinfecting composition. The methods include providing a mixed peroxycarboxylic acid composition comprising: a first ester of a polyhydric alcohol and a C1 to C18 carboxylic acid; a second ester of a polyhydric alcohol and a C1 to C18 carboxylic acid; a source of alkalinity; and an oxidizing agent. The method further includes providing an acidic aqueous solution; and diluting the mixed peroxycarboxylic acid composition with the acidic aqueous solution to a pH of about 1.0 to about 8.0 to form the disinfecting composition.

In other aspects, the present disclosure provides methods for disinfecting a surface comprising contacting the surface with a mixed peroxycarboxylic acid disinfecting composition formed by diluting a composition comprising a first ester of a polyhydric alcohol and a C1 to C18 carboxylic acid, a second ester of a polyhydric alcohol and a C1 to C18 carboxylic acid, a source of alkalinity, and an oxidizing agent, with an aqueous acidic solution to a pH of about 1 to about 8.

In still yet other aspects, the present disclosure provides methods for forming a disinfecting composition. The methods include providing a peroxycarboxylic acid composition comprising: an ester of a polyhydric alcohol and a C1 to C18 carboxylic acid; a source of alkalinity; and an oxidizing agent; wherein said composition has a pH greater than 12. The method further includes providing an acidic aqueous solution; and diluting the peroxycarboxylic acid composition with the acidic aqueous solution to a pH of about 1.0 to about 8.0 to form the disinfecting composition.

In other aspects, the present disclosure relates to methods for forming a percarboxylic acid composition. The methods include providing a reaction mixture comprising: an ester of a polyhydric alcohol and a C1 to C18 carboxylic acid; a source of

alkalinity; and an oxidizing agent, wherein the reaction mixture has a pH greater than about 12. The method further includes allowing the reaction mixture to react for a sufficient amount of time such that a C1 to C18 percarboxylic acid is formed.

In other aspects, the present disclosure provides methods for forming a mixed percarboxylic acid composition. The methods include providing a reaction mixture comprising: a first ester of a polyhydric alcohol and a C1 to C18 carboxylic acid; a source of alkalinity; and an oxidizing agent. The methods further include allowing the reaction mixture to react for a sufficient amount of time, and then adding a second ester of a polyhydric alcohol and a C1 to C18, and after addition of the second ester allowing the mixture to react for a sufficient amount of time such that a mixed peroxycarboxylic acid composition is formed.

BRIEF DESCRIPTION OF DRAWINGS

Figure 1 is a graphical depiction of the stability of various peroxycarboxylic acid compositions formed from esters at an alkaline pH over time.

DETAILED DESCRIPTION

The present disclosure relates to peroxycarboxylic acid compositions generated in situ from a non-equilibrium ester based reaction, as well as methods of making and using such compositions. The compositions disclosed herein have many advantages over conventional, equilibrium based peroxycarboxylic acid compositions. For example, after peroxycarboxylic acid formation according to methods disclosed herein, the compositions have significantly lower levels of reactants compared to peroxycarboxylic acid compositions

generated using equilibrium reactions. Further, as the compositions are generated in situ, and can be generated on site, the compositions can be substantially free of, or even free of, stabilizers. Additionally, due to the ability to generate the disclosed peroxycarboxylic acid compositions on site, the step of shipping hazardous peroxycarboxylic acid compositions to an end user can be eliminated.

So that the present invention may be more readily understood, certain terms are first defined.

As used herein, the terms "mixed" or "mixture" when used relating to "peroxycarboxylic acid composition" or "peroxycarboxylic acids" refer to a composition or mixture including more than one peroxycarboxylic acid, such as a composition or mixture including peroxyacetic acid and peroxyoctanoic acid.

As used herein, the terms "peracid," "peroxy acid" or "peroxy acid" refer to an acid having an acid hydroxyl group replaced by a –OOH group. Oxidizing peracids are referred to herein as peroxycarboxylic acids.

As used herein, the phrases "objectionable odor," "offensive odor," or "malodor," refer to a sharp, pungent, or acrid odor or atmospheric environment from which a typical person withdraws if they are able to. Hedonic tone provides a measure of the degree to which an odor is pleasant or unpleasant. An "objectionable odor," "offensive odor," or "malodor" has an hedonic tone rating it as unpleasant as or more unpleasant than a solution of 5 wt-% acetic acid, propionic acid, butyric acid, or mixtures thereof.

As used herein, the term "microorganism" refers to any noncellular or unicellular (including colonial) organism. Microorganisms include all prokaryotes. Microorganisms include bacteria (including cyanobacteria), spores, lichens, fungi, protozoa, virinos, viroids,

viruses, phages, and some algae. As used herein, the term “microbe” is synonymous with microorganism.

As used herein, the phrase "food product" includes any food substance that might require treatment with an antimicrobial agent or composition and that is edible with or without further preparation. Food products include meat (e.g. red meat and pork), seafood, poultry, produce (e.g., fruits and vegetables), eggs, living eggs, egg products, ready to eat food, wheat, seeds, roots, tubers, leafs, stems, corns, flowers, sprouts, seasonings, or a combination thereof. The term "produce" refers to food products such as fruits and vegetables and plants or plant-derived materials that are typically sold uncooked and, often, unpackaged, and that can sometimes be eaten raw.

As used herein, the phrase “plant” or "plant product" includes any plant substance or plant-derived substance. Plant products include, but are not limited to, seeds, nuts, nut meats, cut flowers, plants or crops grown or stored in a greenhouse, house plants, and the like. Plant products include many animal feeds.

As used herein, the phrase “meat product” refers to all forms of animal flesh, including the carcass, muscle, fat, organs, skin, bones and body fluids and like components that form the animal. Animal flesh includes, but is not limited to, the flesh of mammals, birds, fishes, reptiles, amphibians, snails, clams, crustaceans, other edible species such as lobster, crab, etc., or other forms of seafood. The forms of animal flesh include, for example, the whole or part of animal flesh, alone or in combination with other ingredients. Typical forms include, for example, processed meats such as cured meats, sectioned and formed products, minced products, finely chopped products, ground meat and products including ground meat, whole products, and the like.

As used herein the term "poultry" refers to all forms of any bird kept, harvested, or domesticated for meat or eggs, and including chicken, turkey, ostrich, game hen, squab, guinea fowl, pheasant, quail, duck, goose, emu, or the like and the eggs of these birds. Poultry includes whole, sectioned, processed, cooked or raw poultry, and encompasses all forms of poultry flesh, by-products, and side products. The flesh of poultry includes muscle, fat, organs, skin, bones and body fluids and like components that form the animal. Forms of animal flesh include, for example, the whole or part of animal flesh, alone or in combination with other ingredients. Typical forms include, for example, processed poultry meat, such as cured poultry meat, sectioned and formed products, minced products, finely chopped products and whole products.

As used herein, the phrase "poultry debris" refers to any debris, residue, material, dirt, offal, poultry part, poultry waste, poultry viscera, poultry organ, fragments or combinations of such materials, and the like removed from a poultry carcass or portion during processing and that enters a waste stream.

As used herein, the phrase “food processing surface” refers to a surface of a tool, a machine, equipment, a structure, a building, or the like that is employed as part of a food processing, preparation, or storage activity. Examples of food processing surfaces include surfaces of food processing or preparation equipment (e.g., slicing, canning, or transport equipment, including flumes), of food processing wares (e.g., utensils, dishware, wash ware, and bar glasses), and of floors, walls, or fixtures of structures in which food processing occurs. Food processing surfaces are found and employed in food anti-spoilage air circulation systems, aseptic packaging sanitizing, food refrigeration and cooler cleaners and sanitizers, ware washing sanitizing, blancher cleaning and sanitizing, food packaging

materials, cutting board additives, third-sink sanitizing, beverage chillers and warmers, meat chilling or scalding waters, autodish sanitizers, sanitizing gels, cooling towers, food processing antimicrobial garment sprays, and non-to-low-aqueous food preparation lubricants, oils, and rinse additives.

As used herein, the term "ware" refers to items such as eating and cooking utensils, dishes, and other hard surfaces such as showers, sinks, toilets, bathtubs, countertops, windows, mirrors, transportation vehicles, and floors. As used herein, the term "warewashing" refers to washing, cleaning, or rinsing ware. Ware also refers to items made of plastic. Types of plastics that can be cleaned with the compositions according to the invention include but are not limited to, those that include polycarbonate polymers (PC), acrilonitrile-butadiene-styrene polymers (ABS), and polysulfone polymers (PS). Another exemplary plastic that can be cleaned using the compounds and compositions of the invention include polyethylene terephthalate (PET).

As used herein, the phrase "air streams" includes food anti-spoilage air circulation systems. Air streams also include air streams typically encountered in hospital, surgical, infirmity, birthing, mortuary, and clinical diagnosis rooms.

As used herein, the term "waters" includes food process or transport waters. Food process or transport waters include produce transport waters (e.g., as found in flumes, pipe transports, cutters, slicers, blanchers, retort systems, washers, and the like), belt sprays for food transport lines, boot and hand-wash dip-pans, third-sink rinse waters, and the like. Waters also include domestic and recreational waters such as pools, spas, recreational flumes and water slides, fountains, and the like.

As used herein, the phrase "health care surface" refers to a surface of an instrument, a device, a cart, a cage, furniture, a structure, a building, or the like that is employed as part of a health care activity. Examples of health care surfaces include surfaces of medical or dental instruments, of medical or dental devices, of electronic apparatus employed for monitoring patient health, and of floors, walls, or fixtures of structures in which health care occurs. Health care surfaces are found in hospital, surgical, infirmity, birthing, mortuary, and clinical diagnosis rooms. These surfaces can be those typified as "hard surfaces" (such as walls, floors, bed-pans, etc.,), or fabric surfaces, e.g., knit, woven, and non-woven surfaces (such as surgical garments, draperies, bed linens, bandages, etc.,), or patient-care equipment (such as respirators, diagnostic equipment, shunts, body scopes, wheel chairs, beds, etc.,), or surgical and diagnostic equipment. Health care surfaces include articles and surfaces employed in animal health care.

As used herein, the term "instrument" refers to the various medical or dental instruments or devices that can benefit from cleaning with a composition according to the present invention.

As used herein, the phrases "medical instrument," "dental instrument," "medical device," "dental device," "medical equipment," or "dental equipment" refer to instruments, devices, tools, appliances, apparatus, and equipment used in medicine or dentistry. Such instruments, devices, and equipment can be cold sterilized, soaked or washed and then heat sterilized, or otherwise benefit from cleaning in a composition of the present invention. These various instruments, devices and equipment include, but are not limited to: diagnostic instruments, trays, pans, holders, racks, forceps, scissors, shears, saws (e.g. bone saws and their blades), hemostats, knives, chisels, rongeurs, files, nippers, drills, drill bits, rasps,

burrs, spreaders, breakers, elevators, clamps, needle holders, carriers, clips, hooks, gouges, curettes, retractors, straightener, punches, extractors, scoops, keratomes, spatulas, expressors, trocars, dilators, cages, glassware, tubing, catheters, cannulas, plugs, stents, scopes (e.g., endoscopes, stethoscopes, and arthoscopes) and related equipment, and the like, or combinations thereof.

As used herein, "agricultural" or "veterinary" objects or surfaces include animal feeds, animal watering stations and enclosures, animal quarters, animal veterinarian clinics (e.g. surgical or treatment areas), animal surgical areas, and the like.

As used herein, the term "phosphorus-free" or "substantially phosphorus-free" refers to a composition, mixture, or ingredient that does not contain phosphorus or a phosphorus-containing compound or to which phosphorus or a phosphorus-containing compound has not been added. Should phosphorus or a phosphorus-containing compound be present through contamination of a phosphorus-free composition, mixture, or ingredients, the amount of phosphorus shall be less than 0.5 wt %. More preferably, the amount of phosphorus is less than 0.1 wt%, and most preferably the amount of phosphorus is less than 0.01 wt %.

For the purpose of this patent application, successful microbial reduction is achieved when the microbial populations are reduced by at least about 50%, or by significantly more than is achieved by a wash with water. Larger reductions in microbial population provide greater levels of protection.

As used herein, the term "sanitizer" refers to an agent that reduces the number of bacterial contaminants to safe levels as judged by public health requirements. In an embodiment, sanitizers for use in this invention will provide at least a 99.999% reduction (5-log order reduction). These reductions can be evaluated using a procedure set out in

Germicidal and Detergent Sanitizing Action of Disinfectants, Official Methods of Analysis of the Association of Official Analytical Chemists, paragraph 960.09 and applicable sections, 15th Edition, 1990 (EPA Guideline 91-2). According to this reference a sanitizer should provide a 99.999% reduction (5-log order reduction) within 30 seconds at room temperature, 25±2°C, against several test organisms.

As used herein, the term "disinfectant" refers to an agent that kills all vegetative cells including most recognized pathogenic microorganisms, using the procedure described in *A.O.A.C. Use Dilution Methods*, Official Methods of Analysis of the Association of Official Analytical Chemists, paragraph 955.14 and applicable sections, 15th Edition, 1990 (EPA Guideline 91-2). As used herein, the term "high level disinfection" or "high level disinfectant" refers to a compound or composition that kills substantially all organisms, except high levels of bacterial spores, and is effected with a chemical germicide cleared for marketing as a sterilant by the Food and Drug Administration. As used herein, the term "intermediate-level disinfection" or "intermediate level disinfectant" refers to a compound or composition that kills mycobacteria, most viruses, and bacteria with a chemical germicide registered as a tuberculocide by the Environmental Protection Agency (EPA). As used herein, the term "low-level disinfection" or "low level disinfectant" refers to a compound or composition that kills some viruses and bacteria with a chemical germicide registered as a hospital disinfectant by the EPA.

As used in this invention, the term "sporicide" refers to a physical or chemical agent or process having the ability to cause greater than a 90% reduction (1-log order reduction) in the population of spores of *Bacillus cereus* or *Bacillus subtilis* within 10 seconds at 60° C. In certain embodiments, the sporicidal compositions of the invention provide greater than a

99% reduction (2-log order reduction), greater than a 99.99% reduction (4-log order reduction), or greater than a 99.999% reduction (5-log order reduction) in such population within 10 seconds at 60° C.

Differentiation of antimicrobial "-cidal" or "-static" activity, the definitions which describe the degree of efficacy, and the official laboratory protocols for measuring this efficacy are considerations for understanding the relevance of antimicrobial agents and compositions. Antimicrobial compositions can affect two kinds of microbial cell damage. The first is a lethal, irreversible action resulting in complete microbial cell destruction or incapacitation. The second type of cell damage is reversible, such that if the organism is rendered free of the agent, it can again multiply. The former is termed microbiocidal and the later, microbistatic. A sanitizer and a disinfectant are, by definition, agents which provide antimicrobial or microbiocidal activity. In contrast, a preservative is generally described as an inhibitor or microbistatic composition

As used herein, the term “alkyl” or “alkyl groups” refers to saturated hydrocarbons having one or more carbon atoms, including straight-chain alkyl groups (e.g., methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, etc.), cyclic alkyl groups (or "cycloalkyl" or "alicyclic" or "carbocyclic" groups) (e.g., cyclopropyl, cyclopentyl, cyclohexyl, cycloheptyl, cyclooctyl, etc.), branched-chain alkyl groups (e.g., isopropyl, tert-butyl, sec-butyl, isobutyl, etc.), and alkyl-substituted alkyl groups (e.g., alkyl-substituted cycloalkyl groups and cycloalkyl-substituted alkyl groups).

Unless otherwise specified, the term “alkyl” includes both “unsubstituted alkyls” and “substituted alkyls.” As used herein, the term “substituted alkyls” refers to alkyl groups having substituents replacing one or more hydrogens on one or more carbons of the

hydrocarbon backbone. Such substituents may include, for example, alkenyl, alkynyl, halogeno, hydroxyl, alkylcarbonyloxy, arylcarbonyloxy, alkoxycarbonyloxy, aryloxy, aryloxycarbonyloxy, carboxylate, alkylcarbonyl, arylcarbonyl, alkoxycarbonyl, aminocarbonyl, alkylaminocarbonyl, dialkylaminocarbonyl, alkylthiocarbonyl, alkoxyl, phosphate, phosphonato, phosphinato, cyano, amino (including alkyl amino, dialkylamino, arylamino, diarylamino, and alkylarylamino), acylamino (including alkylcarbonylamino, arylcarbonylamino, carbamoyl and ureido), imino, sulfhydryl, alkylthio, arylthio, thiocarboxylate, sulfates, alkylsulfinyl, sulfonates, sulfamoyl, sulfonamido, nitro, trifluoromethyl, cyano, azido, heterocyclic, alkylaryl, or aromatic (including heteroaromatic) groups.

In some embodiments, substituted alkyls can include a heterocyclic group. As used herein, the term “heterocyclic group” includes closed ring structures analogous to carbocyclic groups in which one or more of the carbon atoms in the ring is an element other than carbon, for example, nitrogen, sulfur or oxygen. Heterocyclic groups may be saturated or unsaturated. Exemplary heterocyclic groups include, but are not limited to, aziridine, ethylene oxide (epoxides, oxiranes), thiirane (episulfides), dioxirane, azetidine, oxetane, thietane, dioxetane, dithietane, dithiete, azolidine, pyrrolidine, pyrroline, oxolane, dihydrofuran, and furan.

As used herein, "weight percent," "wt-%," "percent by weight," "% by weight," and variations thereof refer to the concentration of a substance as the weight of that substance divided by the total weight of the composition and multiplied by 100. It is understood that,

as used here, "percent," "%," and the like are intended to be synonymous with "weight percent," "wt-%," etc.

As used herein, the term "about" refers to variation in the numerical quantity that can occur, for example, through typical measuring and liquid handling procedures used for making concentrates or use solutions in the real world; through inadvertent error in these procedures; through differences in the manufacture, source, or purity of the ingredients used to make the compositions or carry out the methods; and the like. The term "about" also encompasses amounts that differ due to different equilibrium conditions for a composition resulting from a particular initial mixture. Whether or not modified by the term "about", the claims include equivalents to the quantities.

It should be noted that, as used in this specification and the appended claims, the singular forms "a," "an," and "the" include plural referents unless the content clearly dictates otherwise. Thus, for example, reference to a composition containing "a compound" includes a composition having two or more compounds. It should also be noted that the term "or" is generally employed in its sense including "and/or" unless the content clearly dictates otherwise.

In some aspects, the present disclosure relates to a non-equilibrium peroxycarboxylic acid forming composition, and methods of making and using the compositions. Peroxycarboxylic acids are known for use as antimicrobials and bleaching agents. Conventional peroxycarboxylic acid compositions are formed through an acid catalyzed equilibrium reaction. Although acid catalyzed equilibrium reactions are commonly used to generate peroxycarboxylic acids, there are many downsides to such compositions, including,

but not limited to the use of excess amounts of reactants, and hazardous shipping conditions. The present compositions, and methods of forming them, avoid these issues.

Compositions

In some aspects, the present disclosure relates to peroxycarboxylic acid forming compositions. That is, the compositions are capable of generating peroxycarboxylic acids in situ, in a non-equilibrium reaction. Surprisingly, it has been found that peroxycarboxylic acid compositions can be formed at relatively high pH levels, viz. pH greater than 12, or pH greater than 13. It has also been found that mixed peroxycarboxylic acid compositions, viz. compositions that form two or more peroxycarboxylic acids, can be generated in situ in accordance with the methods disclosed herein. Peroxycarboxylic (or percarboxylic) acids generally have the formula $R(CO_3H)n$, where, for example, R is an alkyl, arylalkyl, cycloalkyl, aromatic, or heterocyclic group, and n is one, two, or three, and named by prefixing the parent acid with peroxy. The R group can be saturated or unsaturated as well as substituted or unsubstituted.

In some aspects, the compositions include an ester of a polyhydric alcohol and a C1 to C18 carboxylic acid. The compositions can also include more than one ester of a polyhydric alcohol and a C1 to C18 carboxylic acid. For example, in some embodiments, the compositions include two, three or four esters. When more than one ester is present, the esters can be different. For example, in some embodiments, the compositions can include a first ester of a polyhydric alcohol and a C1 to C4 carboxylic acid, and a second ester of a polyhydric alcohol and a C5 to C11 carboxylic acid.

As used herein, the term "polyhydric alcohol" or "polyol," refers to an alcohol that has two or more hydroxyl groups. Polyhydric alcohols suitable for use in the compositions include, but are not limited to, sugars, sugar alcohols, and mixtures and derivatives thereof.

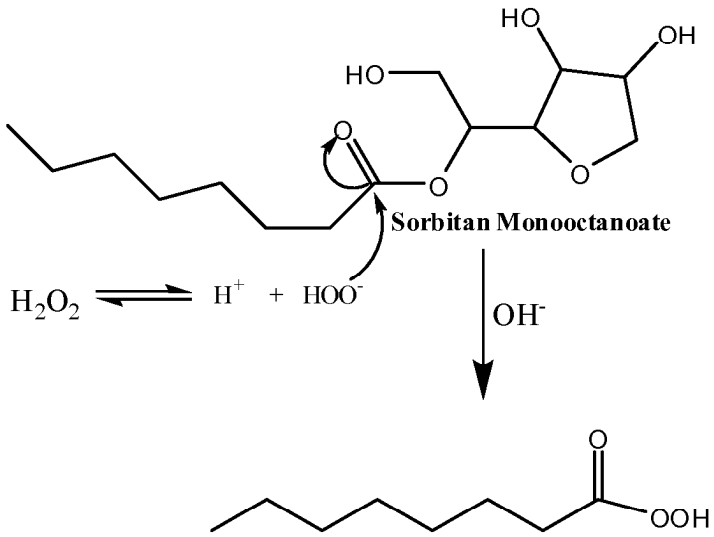
As used herein the term "sugar" refers to carbohydrates including one, two, or more saccharose groups. Sugars are a group of organic compounds related by molecular structure that comprise simpler members of the general class of carbohydrates. Each sugar consists of a chain of 2 to 7 carbon atoms (usually 5 or 6). Sugars have the general formula $C_nH_{2n}O_n$, wherein n is between 2 and 7. One of the carbons carries aldehydic or ketonic oxygen which may be combined in acetal or ketal forms and the remaining carbon atoms usually bear hydrogen atoms and hydroxyl groups. In general, sugars are more or less sweet, water soluble, colorless, odorless, optically active substances which lose water, caramelize and char when heated. Exemplary sugars include, but are not limited to, glucose, sucrose, lactose and mixtures thereof.

The polyhydric alcohol may also include a sugar alcohol. As used herein, the term "sugar alcohol" refers to the hydrogenated form of a carbohydrate, wherein the carbonyl group of the carbohydrate has been reduced to a primary or secondary hydroxyl group. Sugar alcohols have the general formula $CH_2OH(CHOH)_nCH_2OH$, wherein n is from 2 to 5. Exemplary sugar alcohols include, but are not limited to, glycol, ethylene glycol, propylene glycol, glycerol, erythritol, pentaerythritol, threitol, arabitol, xylitol, ribitol, mannitol, sorbitol, sorbitan, dulcitol, iditol, inositol, isomalt, maltitol, lactitol, polyglycitol, 1,4-cyclohexane diol, and mixtures and derivatives thereof. In some embodiments, the sugar alcohol is selected from ethylene glycol, propylene glycol, glycerol, polyglycerol, sorbitol, sorbitan, and mixtures and derivatives thereof.

The esters for use in the present invention include esters of polyhydric alcohols with carboxylic acid based leaving groups. A variety of carboxylic acids can be included. Carboxylic acids generally have the formula R(COOH)n, where, for example, R is an alkyl, arylalkyl, cycloalkyl, aromatic, or heterocyclic group, and n is one, two, or three. In some embodiments, the carboxylic acid leaving group is a C_5 to C_{11} carboxylic acid. In some embodiments, the carboxylic acid leaving group is a C_1 to C_4 carboxylic acid. In other embodiments, the compositions include two esters of polyhydric alcohols, each ester having a different carboxylic acid leaving group. For example, the compositions can include a polyhydric alcohol ester with a C1 to C4 carboxylic acid leaving group, and also include a polyhydric alcohol ester with a C5 to C11 carboxylic acid leaving group.

Examples of suitable carboxylic acids include, but are not limited to, formic, acetic, propionic, butanoic, pentanoic, hexanoic, heptanoic, octanoic, nonanoic, decanoic, undecanoic, dodecanoic, as well as their branched isomers, lactic, maleic, ascorbic, citric, hydroxyacetic, neopentanoic, neoheptanoic, neodecanoic, oxalic, malonic, succinic, glutaric, adipic, pimelic subric acid, and mixtures thereof.

Without wishing to be bound by any particular theory, it is thought that the esters included in the compositions undergo a perhydrolysis reaction, thereby forming the peroxycarboxylic composition. An exemplary perhydrolysis reaction in accordance with the present disclosure is illustrated below:



Peroxyoctanoic Acid

As can be seen from this illustration, it is thought the oxidizing agent, H_2O_2, perhydrolyzes the ester bond, thereby forming the percarboxylic acid corresponding to the cleaved carboxylic acid group. In contrast to an acid catalyzed equilibrium reaction, the reaction is stoichiometric, i.e. no excess amounts of the reactants are required for the reaction. The kinetics of the reaction are pH dependent, and the reaction can reach the maximum yield in the order of minutes. Esters suitable for use include, but are not limited to, monooctanoic glyceride, dioctanoic glyceride, trioctaonoic glyceride, polyglycerol octanoate, sorbitan monooctanoate, sorbitan dioctanoate, sorbitan trioctanoate, laurate sucroside and mixtures and derivatives thereof.

The compositions include the esters in an amount sufficient to generate the desired amount of percarboxylic acid. In some embodiments, the compositions include about 0.01 wt% to about 95 wt% of the ester, about 0.1 wt% to about 50 wt% of the ester, or about 1 wt% to about 10 wt% of the ester. In some embodiments, more than one ester is present in the compositions. Each ester can be present in the compositions at the above stated weight percents.

Unlike conventional acid catalyzed equilibrium peroxycarboxylic acid forming compositions, the compositions of the present invention can be formed using a non-equilibrium perhydrolysis reaction. Thus, an excess amount of the starting reagents is not needed. Accordingly, after formation of the peroxycarboxylic acid, the compositions contain less carboxylic acid and hydrogen peroxide than an equivalent equilibrium reaction. In some embodiments, the compositions contain about 1 part carboxylic acid for every about 1 part peroxycarboxylic acid after perhydrolysis, or about 1 part carboxylic acid for every about 6 part peroxycarboxylic acid after perhydrolysis. In some embodiments, the compositions are free of, or substantially free, of carboxylic acids after the perhydrolysis reaction.

In some embodiments, the compositions contain about 2 parts hydrogen peroxide for every about 1 part peroxycarboxylic acid after perhydrolysis, or about 1 part hydrogen peroxide for every about 5 parts peroxycarboxylic acid after perhydrolysis. In some embodiments, the compositions are free of, or substantially free of, hydrogen peroxide after the perhydrolysis reaction.

The compositions also include a source of alkalinity. The source of alkalinity can include, but is not limited to, an alkaline metal hydroxide, an alkaline earth metal hydroxide, an alkali metal silicate, an alkali metal carbonate, borates and mixtures thereof. Suitable alkaline metal hydroxides include, but are not limited to, sodium hydroxide, potassium hydroxide and mixtures thereof. Suitable alkaline earth metal hydroxides include, but are not limited to, magnesium hydroxide, calcium hydroxide and mixtures and derivatives thereof. Suitable alkali metal silicates include but are not limited to, sodium silicate and derivatives thereof. In other embodiments, an alkali metal carbonate can be used as a source

of alkalinity. For example, in some embodiments, sodium carbonate, sodium bicarbonate or mixtures and derivatives thereof can be used.

The source of alkalinity can be present in the compositions in an amount sufficient to provide the desired pH. In some embodiments, the compositions have a pH greater than about 12, greater than about 12.5, or greater than about 13. In some embodiments, the alkaline source is present in the composition from about 0.001 wt% to about 50 wt%, from about 1wt% to about 30wt%, or about 10wt% to about 25 wt%. In some embodiments, the alkaline source is present at from about 25 wt% to about 50 wt% of the composition. It is to be understood that all ranges and values between these ranges and values are encompassed by the present disclosure.

The compositions also include an oxidizing agent. The oxidizing agent may include a peroxide source. Oxidizing agents suitable for use with the compositions include the following types of compounds or sources of these compounds, or alkali metal salts including these types of compounds, or forming an adduct therewith: hydrogen peroxide, urea-hydrogen peroxide complexes or hydrogen peroxide donors of: group 1 (IA) oxidizing agents, for example lithium peroxide, sodium peroxide; group 2 (IIA) oxidizing agents, for example magnesium peroxide, calcium peroxide, strontium peroxide, barium peroxide; group 12 (IIB) oxidizing agents, for example zinc peroxide; group 13 (IIIA) oxidizing agents, for example boron compounds, such as perborates, for example sodium perborate hexahydrate of the formula $Na_2[B_2(O_2)_2(OH)_4]\cdot 6H_2O$ (also called sodium perborate tetrahydrate); sodium peroxyborate tetrahydrate of the formula $Na_2B_2(O_2)_2[(OH)_4]\cdot 4H_2O$ (also called sodium perborate trihydrate); sodium peroxyborate of the formula $Na_2[B_2(O_2)_2(OH)_4]$ (also called sodium perborate monohydrate); group 14 (IVA) oxidizing

agents, for example persilicates and peroxycarbonates, which are also called percarbonates, such as persilicates or peroxycarbonates of alkali metals; group 15 (VA) oxidizing agents, for example peroxynitrous acid and its salts; peroxyphosphoric acids and their salts, for example, perphosphates; group 16 (VIA) oxidizing agents, for example peroxysulfuric acids and their salts, such as peroxymonosulfuric and peroxydisulfuric acids, and their salts, such as persulfates, for example, sodium persulfate; and group VIIa oxidizing agents such as sodium periodate, potassium perchlorate. Other active inorganic oxygen compounds can include transition metal peroxides; and other such peroxygen compounds, and mixtures thereof.

In some embodiments, the compositions of the present invention employ one or more of the inorganic oxidizing agents listed above. Suitable inorganic oxidizing agents include ozone, hydrogen peroxide, hydrogen peroxide adduct, group IIIA oxidizing agent, or hydrogen peroxide donors of group VIA oxidizing agent, group VA oxidizing agent, group VIIA oxidizing agent, or mixtures thereof. Suitable examples of such inorganic oxidizing agents include percarbonate, perborate, persulfate, perphosphate, persilicate, or mixtures thereof.

In some embodiments, the oxidizing agent includes hydrogen peroxide, or a source or donor of hydrogen peroxide. In other embodiments, the oxidizing agent includes a peroxide source selected from a percarbonate, a perborate urea hydrogen peroxide, PVP-peroxides and mixtures thereof.

The compositions may contain an effective amount of an oxidizing agent. In some embodiments, the compositions include about 0.001 wt% to about 60 wt% of the oxidizing agent, or about 1 wt% to about 25 wt% of the oxidizing agent. In some embodiments, the

compositions include about 30 wt% to about 50 wt% of the oxidizing agent. It is to be understood that all ranges and values between these ranges and values are encompassed by the present invention.

In some embodiments, the compositions of the invention further include a solvent. In some embodiments, the solvent is water. The water may be provided by the use of aqueous reagents, viz. oxidizing agent, alkalinity source. In other embodiments, an additional amount of water is added to the compositions. The compositions may be free of or substantially free of any added water. A non-aqueous solvent may also be used in the compositions. For example, in some embodiments, an alcohol is included as a solvent in the compositions.

The compositions may include an effective amount of solvent. In some embodiments, the compositions may include about 10 wt% to about 99 wt% of a solvent, or about 20 wt % to about 80 wt% of a solvent. In other embodiments, the compositions may include more than about 30 wt%, more than about 50 wt%, more than about 60 wt% or more than 70% of a solvent. It is to be understood that all values and ranges between these values and ranges are encompassed by the present invention.

Unlike conventional equilibrium based peroxycarboxylic acid compositions, the compositions disclosed herein are formed from a non-equilibrium reaction. Further, the composition disclosed herein can be used immediately after generation. Thus, many of the additional ingredients required in equilibrium based compositions do not need to be included in the present compositions. For example, the present compositions can be free of, or substantially free of a stabilizing agent. Stabilizing agents are commonly added to equilibrium peroxycarboxylic acid compositions to stabilize the peracid and hydrogen

peroxide and prevent the decomposition of these constituents within the compositions. The present compositions do not require such stabilizing agents.

Further, unlike conventional equilibrium based peroxycarboxylic acid compositions, the present compositions can also be free of, or substantially free of surfactants. This is especially advantageous for compositions incorporating C5 to C11 peroxycarboxylic acids. That is, under perhydrolysis conditions, the C5-C11 peroxycarboxylic acid anions generated are water soluble. If the anions are acidified for end use applications, the concentrations of peroxycarboxylic acids are below the water solubility limit of the peroxycarboxylic acids. Thus, surfactants are not needed to couple the peroxycarboxylic acids in solution.

The compositions may also include additional functional ingredients. Additional functional ingredients suitable for use in the present compositions include, but are not limited to, acidulants, hydrotropes, antimicrobial agents, optical tracers, solidification agent, aesthetic enhancing agent (i.e., colorant (e.g., pigment), odorant, or perfume), among any number of constituents which can be added to the composition. Such adjuvants can be preformulated with the present compositions or added to the compositions after formation, but prior to use. The compositions can also contain any number of other constituents as necessitated by the application, which are known and which can facilitate the activity of the present compositions.

In an embodiment, the present compositions can include an acidulant. The acidulant can be added to the compositions after the formation of the percarboxylic acid. That is, an acidulant can be added to the peroxycarboxylic acid concentrate to form an acidified use solution. The acidulant can be effective to form a use composition with pH of about 1 or less. The acidulant can be effective to form a use composition with pH of about 8, about 8

or less, about 7, about 7 or less, about 6, about 6 or less, about 5, about 5 or less, or the like. In some embodiments, the acidulant is present at an amount effective to form a use solution with a pH of about 6 to about 8, about 1 to about 8, or about 1 to about 5.

Any suitable acid can be included in the compositions as an acidulant. In an embodiment, the acidulant includes an inorganic acid. Suitable inorganic acids include, but are not limited to, sulfuric acid, sodium bisulfate, phosphoric acid, nitric acid, hydrochloric acid. In some embodiments, the acidulant includes an organic acid. Suitable organic acids include, but are not limited to, methane sulfonic acid, ethane sulfonic acid, propane sulfonic acid, butane sulfonic acid, toluene sulfonic acid, xylene sulfonic acid, cumene sulfonic acid, benzene sulfonic acid, formic acid, acetic acid, mono, di, or tri-halocarboyxlic acids, picolinic acid, dipicolinic acid, and mixtures thereof. In some embodiments, the compositions of the present invention are free or substantially free of a phosphorous based acid.

In an embodiment, the acidulant includes a carboxylic acid with pK_a less than 5. Suitable carboxylic acids with pK_a less than 5 include hydroxyacetic acid, hydroxypropionic acid, other hydroxycarboxylic acids, mixtures thereof, or the like. Such an acidulant is present at a concentration where it does not act as a solubilizer. In some embodiments, the compositions are free of, or substantially free of a carboxylic acid.

In certain embodiments, the present composition includes about 0.001 to about 50 wt-% acidulant, about 0.001 to about 30 wt-% acidulant, about 1 to about 50 wt-% acidulant, about 1 to about 30 wt-% acidulant, about 2 to about 40 wt-% acidulant, about 2 to about 10 wt-% acidulant, about 3 to about 40 wt-% acidulant, about 5 to about 40 wt-% acidulant, about 5 to about 25 wt-% acidulant, about 10 to about 40 wt-% acidulant, about 10 to about

30 wt-% acidulant, about 15 to about 35 wt-% acidulant, about 15 to about 30 wt-% acidulant, or about 40 to about 60 wt-% acidulant. The composition can include any of these ranges or amounts not modified by about.

Methods for making and using

In some aspects, the present disclosure provides methods for making the peroxycarboxylic acid compositions disclosed herein. The method includes combining at least one ester of a polyhydric alcohol and a C1 to C18 carboxylic acid, a source of alkalinity and an oxidizing agent. This reaction mixture allows for the perhydrolysis of the ester to form the corresponding C1 to C18 peroxycarboxylic acid. Without wishing to be bound by any particular theory it is thought that the oxidizing agent present perhydrolyzes the ester bonds, thereby forming the corresponding percarboxylic acids.

In some embodiments, the pH of the reaction mixture is greater than about 12. In other embodiments, the reaction mixture is greater than about 12.5, or greater than about 13.

The reagents can be combined in any suitable manner. For example, the reagents can be sequentially added to a reaction vessel, and mixed for an amount of time effective to form the desired percarboxylic acid concentration. Alternatively, the reagents can be added substantially simultaneously to a reaction vessel, and mixed for an amount of time effective to form the desired percarboxylic acid concentration. In some embodiments, the reagents are mixed for about 5 to about 30 minutes. In other embodiments, the reagents are mixed for about 10, about 15, about 20, or about 25 minutes.

In some embodiments, a mixed percarboxylic acid composition is formed by using more than one ester of a polyhydric alcohol and a C1 to C18 carboxylic acid as starting reagents. For example, in some embodiments, a mixed percarboxylic acid composition

including peracetic acid and peroctanoic acid is formed. To form this composition, an ester of a polyhydric alcohol and a C2 carboxylic acid is combined with an ester of a polyhydric alcohol and a C8 carboxylic acid, a source of alkalinity, and an oxidizing agent.

When forming a mixed peracid composition, the order of addition can be varied depending on the reaction conditions. For example, in some embodiments, all of the reagents can be combined and mixed in one step. Alternatively, in some embodiments, one of the esters can be added to a reaction vessel, with an oxidizing agent, and a source of alkalinity added sequentially. This mixture can be allowed to react for an effective amount of time, prior to the second ester being added to the reaction mixture. Preparing the mixed percarboxylic acid system in a stepwise manner also allows for control of the reaction temperature. For example, by splitting the perhydrolysis reactions into two steps, the overall temperature of the reaction mixture is lower.

The order of addition and time for reaction can be varied according to the desired percarboxylic acid composition. That is, the reaction can be controlled so as to favor the reaction conditions for formation of each of the percarboxylic acids individually. For example, if it is known that one of the esters has a kinetically slower perhydrolysis reaction rate, that ester can be added to the reaction vessel first. After an amount of time sufficient to maximize the percarboxylic acid formation of the first ester, the second ester with a kinetically faster perhydrolysis reaction rate can be added to the reaction vessel.

In some aspects, the present disclosure provides methods for forming a disinfecting composition. The methods include providing a mixed peroxycarboxylic acid forming composition. The mixed peroxycarboxylic acid forming composition includes: a first ester of a polyhydric alcohol and a C1 to C18 carboxylic acid, for example a C1 to C4 carboxylic

acid; a second ester of a polyhydric alcohol and a C1 to C18 carboxylic acid, for example a C8 to C11 carboxylic acid; a source of alkalinity; and an oxidizing agent. After allowing the reaction mixture to react for a sufficient amount of time, a mixed percarboxylic acid composition is formed. The mixed peroxycarboxylic acid composition is diluted with an acidic aqueous solution. In some embodiments, the mixed peroxycarboxylic acid composition is diluted with an amount of an acidic aqueous solution effective to provide the diluted disinfecting composition with a pH of about 1.0 to about 8.0.

In other aspects, the present disclosure provides methods for forming a disinfecting composition including a single percarboxylic acid. The methods include providing a peroxycarboxylic acid forming composition. The composition includes: an ester of a polyhydric alcohol and a C1 to C18 carboxylic acid; a source of alkalinity; and an oxidizing agent, wherein said composition has a pH greater than 12. The peroxycarboxylic acid forming composition is then diluted with an acidic aqueous solution. In some embodiments, the diluted acidic peroxycarboxylic acid composition has a pH of about 1.0 to about 8.0.

Any acidic solution can be used to dilute the peroxycarboxylic acid compositions. In an embodiment, the acidulant includes an inorganic acid. Suitable inorganic acids include, but are not limited to, sulfuric acid, sodium bisulfate, phosphoric acid, nitric acid, hydrochloric acid. In some embodiments, the acidulant includes an organic acid. Suitable organic acids include, but are not limited to, methane sulfonic acid, ethane sulfonic acid, propane sulfonic acid, butane sulfonic acid, xylene sulfonic acid, cumene sulfonic acid, benzene sulfonic acid, formic acid, acetic acid, mono, di, or tri-halocarboyxlic acids, picolinic acid, dipicolinic acid, and mixtures thereof. In some embodiments, the

compositions of the present invention are free or substantially free of a phosphorous based acid.

In some aspects, the present disclosure includes methods of using the peroxycarboxylic acid forming compositions disclosed herein. In some embodiments, these methods employ the antimicrobial and/or bleaching activity of the compositions. For example, the invention includes a method for reducing a microbial population, a method for reducing the population of a microorganism on skin, a method for treating a disease of skin, a method for reducing an odor, and/or a method for bleaching. These methods can operate on an article, surface, in a body or stream of water or a gas, or the like, by contacting the article, surface, body, or stream with the compositions. Contacting can include any of numerous methods for applying the compositions, such as spraying the compositions, immersing the article in the compositions, foam or gel treating the article with the compositions, or a combination thereof.

In some aspects, the compositions are present at an amount effective for killing one or more of the food-borne pathogenic bacteria associated with a food product, including, but not limited to, *Salmonella typhimurium*, *Salmonella javiana*, *Campylobacter jejuni*, *Listeria monocytogenes*, and *Escherichia coli* O157:H7, yeast, and mold. In some embodiments, the compositions are present at an amount effective for killing one or more of the pathogenic bacteria associated with a health care surfaces and environments including, but not limited to, *Salmonella typhimurium*, *Staphylococcus aureus*, methicilin resistant *Staphylococcus aureus, Salmonella choleraesurus*, *Pseudomonas aeruginosa*, *Escherichia coli*, mycobacteria, yeast, and mold. The compositions of the present invention have activity against a wide variety of microorganisms such as Gram positive (for example, *Listeria*

monocytogenes or *Staphylococcus aureus*) and Gram negative (for example, *Escherichia coli* or *Pseudomonas aeruginosa*) bacteria, yeast, molds, bacterial spores, viruses, etc. The compositions, as described above, have activity against a wide variety of human pathogens. The present compositions can kill a wide variety of microorganisms on a food processing surface, on the surface of a food product, in water used for washing or processing of food product, on a health care surface, or in a health care environment.

The compositions can be used for a variety of domestic or industrial applications, e.g., to reduce microbial or viral populations on a surface or object or in a body or stream of water. The compositions can be applied in a variety of areas including kitchens, bathrooms, factories, hospitals, dental offices and food plants, and can be applied to a variety of hard or soft surfaces having smooth, irregular or porous topography. Suitable hard surfaces include, for example, architectural surfaces (e.g., floors, walls, windows, sinks, tables, counters and signs); eating utensils; hard-surface medical or surgical instruments and devices; and hard-surface packaging. Such hard surfaces can be made from a variety of materials including, for example, ceramic, metal, glass, wood or hard plastic. Suitable soft surfaces include, for example paper; filter media; hospital and surgical linens and garments; soft-surface medical or surgical instruments and devices; and soft-surface packaging. Such soft surfaces can be made from a variety of materials including, for example, paper, fiber, woven or nonwoven fabric, soft plastics and elastomers. The compositions of the invention can also be applied to soft surfaces such as food and skin (e.g., a hand). The present compositions can be employed as a foaming or nonfoaming environmental sanitizer or disinfectant.

The compositions of the invention can be included in products such as sterilants, sanitizers, disinfectants, preservatives, deodorizers, antiseptics, fungicides, germicides,

sporicides, virucides, detergents, bleaches, hard surface cleaners, hand soaps, waterless hand sanitizers, and pre- or post-surgical scrubs.

The compositions can also be used in veterinary products such as mammalian skin treatments or in products for sanitizing or disinfecting animal enclosures, pens, watering stations, and veterinary treatment areas such as inspection tables and operation rooms. The present compositions can be employed in an antimicrobial foot bath for livestock or people. The compositions can also be employed as an antimicrobial teat dip.

The compositions can also be used on foods and plant species to reduce surface microbial populations; used at manufacturing or processing sites handling such foods and plant species; or used to treat process waters around such sites. For example, the compositions can be used on food transport lines (e.g., as belt sprays); boot and hand-wash dip-pans; food storage facilities; anti-spoilage air circulation systems; refrigeration and cooler equipment; beverage chillers and warmers, blanchers, cutting boards, third sink areas, and meat chillers or scalding devices. The compositions can be used to treat produce transport waters such as those found in flumes, pipe transports, cutters, slicers, blanchers, retort systems, washers, and the like. Particular foodstuffs that can be treated with compositions of the invention include eggs, meats, seeds, leaves, fruits and vegetables. Particular plant surfaces include both harvested and growing leaves, roots, seeds, skins or shells, stems, stalks, tubers, corms, fruit, and the like. The compositions may also be used to treat animal carcasses to reduce both pathogenic and non-pathogenic microbial levels.

The compositions can also be used to treat waste water where both its antimicrobial function and its oxidant properties can be utilized. Aside from the microbial issues surrounding waste water, it is often rich in malodorous compounds of reduced sulfur,

nitrogen or phosphorous. A strong oxidant such as the present invention converts these compounds efficiently to their odor free derivatives e.g. the sulfates, phosphates and amine oxides. These same properties are very useful in the pulp and paper industry where the property of bleaching is also of great utility.

In some aspects, the compositions of the present invention are useful in the cleaning or sanitizing of containers, processing facilities, or equipment in the food service or food processing industries. The compositions have particular value for use on food packaging materials and equipment, and especially for cold or hot aseptic packaging. Examples of process facilities in which the compositions can be employed include a milk line dairy, a continuous brewing system, food processing lines such as pumpable food systems and beverage lines, etc. Food service wares can be disinfected with the compositions. For example, the compositions can also be used on or in ware wash machines, low temperature ware wash machines, dishware, bottle washers, bottle chillers, warmers, third sink washers, cutting areas (e.g., water knives, slicers, cutters and saws) and egg washers. Particular treatable surfaces include packaging such as cartons, bottles, films and resins; dish ware such as glasses, plates, utensils, pots and pans; ware wash and low temperature ware wash machines; exposed food preparation area surfaces such as sinks, counters, tables, floors and walls; processing equipment such as tanks, vats, lines, pumps and hoses (e.g., dairy processing equipment for processing milk, cheese, ice cream and other dairy products); and transportation vehicles. Containers include glass bottles, PVC or polyolefin film sacks, cans, polyester, PEN or PET bottles of various volumes (100 ml to 2 liter, etc.), one gallon milk containers, paper board juice or milk containers, etc.

The compositions can also be used on or in other industrial equipment and in other industrial process streams such as heaters, cooling towers, boilers, retort waters, rinse waters, aseptic packaging wash waters, and the like. The compositions can be used to treat microbes and odors in recreational waters such as in pools, spas, recreational flumes and water slides, fountains, and the like.

The compositions can also be employed by dipping food processing equipment into the use solution, soaking the equipment for a time sufficient to sanitize the equipment, and wiping or draining excess solution off the equipment, The compositions may be further employed by spraying or wiping food processing surfaces with the use solution, keeping the surfaces wet for a time sufficient to sanitize the surfaces, and removing excess solution by wiping, draining vertically, vacuuming, etc.

The compositions may also be used in a method of sanitizing hard surfaces such as institutional type equipment, utensils, dishes, health care equipment or tools, and other hard surfaces.

A concentrate or use concentration of the compositions can be applied to or brought into contact with an object by any conventional method or apparatus for applying an antimicrobial or cleaning compound to an object. For example, the object can be wiped with, sprayed with, foamed on, and/or immersed in the compositions, or a use solution made from the compositions. The compositions can be sprayed, foamed, or wiped onto a surface; the compositions can be caused to flow over the surface, or the surface can be dipped into the compositions. Contacting can be manual or by machine. Food processing surfaces, food products, food processing or transport waters, and the like can be treated with liquid, foam,

gel, aerosol, gas, wax, solid, or powdered stabilized compositions according to the invention, or solutions containing these compounds.

Other hard surface cleaning applications for the compositions include clean-in-place systems (CIP), clean-out-of-place systems (COP), washer-decontaminators, sterilizers, textile laundry machines, ultra and nano-filtration systems and indoor air filters. COP systems can include readily accessible systems including wash tanks, soaking vessels, mop buckets, holding tanks, scrub sinks, vehicle parts washers, non-continuous batch washers and systems, and the like. CIP systems include the internal components of tanks, lines, pumps and other process equipment used for processing typically liquid product streams such as beverages, milk, juices.

A method of sanitizing substantially fixed in-place process facilities includes the following steps. A composition in accordance with various embodiments of the invention is introduced into the process facilities at a temperature in the range of about 4 ºC to 60 ºC. After introduction of the composition, the solution is held in a container or circulated throughout the system for a time sufficient to sanitize the process facilities (e.g., to kill undesirable microorganisms). After the surfaces have been sanitized by means of the present compositions, the solution is drained. Upon completion of the sanitizing step, the system optionally may be rinsed with other materials such as potable water. The compositions can be circulated through the process facilities for 10 minutes or less.

The present methods can include delivering the present composition via air delivery to the clean-in-place or other surfaces such as those inside pipes and tanks. This method of air delivery can reduce the volume of solution required.

Methods for Contacting a Food Product

In some aspects, the present invention provides methods for contacting a food product with compositions according to the invention employing any method or apparatus suitable for applying such compositions. For example, in some embodiments, the food product is contacted by the compositions with a spray of the compositions, by immersion in the compositions, by foam or gel treating with the compositions. Contact with a spray, a foam, a gel, or by immersion can be accomplished by a variety of methods known to those of skill in the art for applying antimicrobial agents to food. Contacting the food product can occur in any location in which the food product might be found, such as field, processing site or plant, vehicle, warehouse, store, restaurant, or home. These same methods can also be adapted to apply the compositions of the present invention to other objects.

The present methods require a certain minimal contact time of the compositions with food product for occurrence of significant antimicrobial effect. The contact time can vary with concentration of the use compositions, method of applying the use compositions, temperature of the use compositions, amount of soil on the food product, number of microorganisms on the food product, type of antimicrobial agent, or the like. The exposure time can be at least about 5 to about 15 seconds. In some embodiments, the exposure time is about 15 to about 30 seconds. In other embodiments, the exposure time is at least about 30 seconds.

In some embodiments, the method for washing a food product employs a pressure spray including compositions of the present invention. During application of the spray solution on the food product, the surface of the food product can be moved with mechanical action, e.g., agitated, rubbed, brushed, etc. Agitation can be by physical scrubbing of the

food product, through the action of the spray solution under pressure, through sonication, or by other methods. Agitation increases the efficacy of the spray solution in killing micro-organisms, perhaps due to better exposure of the solution into the crevasses or small colonies containing the micro-organisms. The spray solution, before application, can also be heated to a temperature of about 15 to 20 °C, for example, about 20 to 60 °C to increase efficacy. The spray stabilized compositions can be left on the food product for a sufficient amount of time to suitably reduce the population of microorganisms, and then rinsed, drained, or evaporated off the food product.

Application of the material by spray can be accomplished using a manual spray wand application, an automatic spray of food product moving along a production line using multiple spray heads to ensure complete contact, or other spray apparatus. One automatic spray application involves the use of a spray booth. The spray booth substantially confines the sprayed compositions to within the booth. The production line moves the food product through the entryway into the spray booth in which the food product is sprayed on all its exterior surfaces with sprays within the booth. After a complete coverage of the material and drainage of the material from the food product within the booth, the food product can then exit the booth. The spray booth can include steam jets that can be used to apply the stabilized compounds of the invention. These steam jets can be used in combination with cooling water to ensure that the treatment reaching the food product surface is less than 65°C, e.g., less than 60°C. The temperature of the spray on the food product is important to ensure that the food product is not substantially altered (cooked) by the temperature of the spray. The spray pattern can be virtually any useful spray pattern.

Immersing a food product in the liquid compositions of the present invention can be accomplished by any of a variety of methods known to those of skill in the art. For example, the food product can be placed into a tank or bath containing the compositions. Alternatively, the food product can be transported or processed in a flume of the compositions. The washing solution can be agitated to increase the efficacy of the solution and the speed at which the solution reduces micro-organisms accompanying the food product. Agitation can be obtained by conventional methods, including ultrasonics, aeration by bubbling air through the solution, by mechanical methods, such as strainers, paddles, brushes, pump driven liquid jets, or by combinations of these methods. The washing solution can be heated to increase the efficacy of the solution in killing micro-organisms. After the food product has been immersed for a time sufficient for the desired antimicrobial effect, the food product can be removed from the bath or flume and the compositions can be rinsed, drained, or evaporated off the food product.

In other embodiments, a food product can be treated with a foaming version of the compositions of the present invention. The foam can be prepared by mixing foaming surfactants with the washing solution at time of use. The foaming surfactants can be nonionic, anionic or cationic in nature. Examples of useful surfactant types include, but are not limited to the following: alcohol ethoxylates, alcohol ethoxylate carboxylate, amine oxides, alkyl sulfates, alkyl ether sulfate, sulfonates, including, for example, alkyl aryl sulfonates, quaternary ammonium compounds, alkyl sarcosines, betaines and alkyl amides. The foaming surfactant is typically mixed at time of use with the washing solution. Use solution levels of the foaming agents is from about 50 ppm to about 2.0 wt-%. At time of use, compressed air can be injected into the mixture, then applied to the food product surface

through a foam application device such as a tank foamer or an aspirated wall mounted foamer.

In some embodiments, a food product can be treated with a thickened or gelled version of the compositions of the present invention. In the thickened or gelled state the washing solution remains in contact with the food product surface for longer periods of time, thus increasing the antimicrobial efficacy. The thickened or gelled solution will also adhere to vertical surfaces. The compositions can be thickened or gelled using existing technologies such as: xanthan gum, polymeric thickeners, cellulose thickeners, or the like. Rod micelle forming systems such as amine oxides and anionic counter ions could also be used. The thickeners or gel forming agents can be used either in the concentrated product or mixing with the washing solution, at time of use. Typical use levels of thickeners or gel agents range from about 100 ppm to about 10 wt-%.

Methods for Beverage, Food, and Pharmaceutical Processing

The compositions of the present invention can be used in the manufacture of beverage, food, and pharmaceutical materials including fruit juice, dairy products, malt beverages, soybean-based products, yogurts, baby foods, bottled water products, teas, cough medicines, drugs, and soft drinks. The compositions of the present invention can be used to sanitize, disinfect, act as a sporicide for, or sterilize bottles, pumps, lines, tanks and mixing equipment used in the manufacture of such beverages. Further, the compositions of the present invention can be used in aseptic, cold filling operations in which the interior of the food, beverage, or pharmaceutical container is sanitized or sterilized prior to filling. In such operations, a container can be contacted with the compositions, typically using a spray,

dipping, or filling device to intimately contact the inside of the container with the compositions, for a sufficient period of time to reduce microorganism populations within the container. The container can then be emptied of the amount of sanitizer or sterilant used. After emptying, the container can be rinsed with potable water or sterilized water and again emptied. After rinsing, the container can be filled with the beverage, food, or pharmaceutical. The container can then be sealed, capped or closed and then packed for shipment for ultimate sale. The sealed container can be autoclaved or retorted for added microorganism kill.

In food, beverage, or pharmaceutical manufacturing, fungal microorganisms of the genus *Chaetomium* or *Arthrinium,* and spores or bacteria of the genus *Bacillus spp.* can be a significant problem in bottling processes, particularly in cold aseptic bottling processes. The compositions of the present invention can be used for the purpose of controlling or substantially reducing (by more than a 5 $\log_{10}$ reduction) the number of *Chaetomium* or *Arthrinium* or *Bacillus* microorganisms in beverage or food or pharmaceutical bottling lines using cold aseptic bottling techniques.

In such techniques, metallic, aluminum or steel cans can be filled, glass bottles or containers can be filled, or plastic (PET or PBT or PEN) bottles, and the like can be filled using cold aseptic filling techniques. In such processes, the compositions of the invention can be used to sanitize the interior of beverage containers prior to filling with the carbonated (or noncarbonated) beverage. Typical carbonated beverages in this application include, but are not limited to, cola beverages, fruit beverages, ginger ale beverages, root beer beverages, iced tea beverages which may be non-carbonated, and other common beverages considered soft drinks. The compositions of the invention can be used to sanitize both the tanks, lines,

pumps, and other equipment used for the manufacture and storage of the soft drink material and also used in the bottling or containers for the beverages. In an embodiment, the compositions are useful for killing both bacterial and fungal microorganisms that can be present on the surfaces of the production equipment and beverage containers.

Those skilled in the art will recognize, or be able to ascertain using no more than routine experimentation, numerous equivalents to the specific procedures, embodiments, claims, and examples described herein. Such equivalents are considered to be within the scope of this invention and covered by the claims appended hereto. The contents of all references, patents, and patent applications cited throughout this application are hereby incorporated by reference. The invention is further illustrated by the following examples, which should not be construed as further limiting.

EXAMPLES

Example 1 –

A study was run to determine the ability to form peroxycarboxylic acids in situ from ester starting materials at alkaline pH levels. For this study, two different peroxycarboxylic acid forming compositions were each studied at two different pH levels. First, a peracetic acid (POAA) forming composition was tested at pH 12 and pH 13. For this test, 1.89grams of hydrogen peroxide was mixed in a beaker with 0.62 grams of triacetin, 15 grams of distilled water, and 7.75grams of a 10% solution of sodium hydroxide (NaOH). The beaker was fitted with a pH probe. After the sodium hydroxide was added the pH went up to about 12 immediately, and remained relatively stable while the sampling was performed. The peroxycarboxylic acid concentration was measured by removing a sample aliquot of the test solution, acidifying it with acetic acid, and titrating it by an iodometric method. Both the peroxycarboxylic acid concentration and the hydrogen peroxide concentrations were measured over time. The above procedure was then repeated using an additional 11.71 grams of a 10% sodium hydroxide solution. This raised the pH to about 13 initially.

The above procedures were repeated twice using sorbitan caprylate instead of triacetin, to generate peroxyoctanoic acid (POOA) in situ. The peroxyoctanoic acid was also generated at both pH 12 and pH 13. The peroxycarboxylic acid concentration and hydrogen peroxide concentration of these test solutions was also measured over time. The results are shown in Figure 1.

As can be seen in Figure 1, the peroxyoctanoic acid generating solution was far more stable than the peracetic acid generating solution over time. This held true even for the

elevated pH 13 test. Thus, as can be seen from this data, peroxyoctanoic acid can be generated in situ at relatively high pH levels, viz. pH about 13.

Example 2 –

A study was performed to evaluate the ability to generate a mixed peroxycarboxylic acid composition in situ from ester starting materials at alkaline pHs. For this study, 1.28 grams of sorbitan octanoate, 14.68 grams of water, and 3.66 grams of a 35% hydrogen peroxide solution were added in a 100 mL beaker. With magnetic stirring, 14.64 grams of a 10% sodium hydroxide solution was added to the beaker. The solution was mixed for ten minutes. Then, 1.70grams of triacetin was added to the solution. After mixing for an additional five minutes, the solution was sampled to measure the peroxyacetic (POAA) and peroxyoctanoic (POOA) acid concentrations.

This two step addition process was also compared to a one step process. For the one step process, 1.26 grams of sorbitan octanoate, 1.70grams of triacetin, 14.67 grams o water, and 3.66 grams of a 35% hydrogen peroxide solution were added in a 100 mL beaker. With magnetic stirring, 14.64 grams of a 10% sodium hydroxide solution was added to the beaker. After mixing for 15 minutes, the solution was sampled for POAA and POOA levels. The results for both the two step and the one step reaction methods are shown in the table below.

Table 1.

Reaction Process	Peroxyacetic Acid (wt%)	Peroxyoctanoic Acid (wt%)	Peroxyacetic/ Peroxyocatanoic (wt% as Peroxyacetic acid)	Temperature (maximum)	pH (initial –end)
Two Step	4.32	0.71	4.89	24.6°C	12.19 -11.47

One Step	3.95	0.60	4.33	28.1°C	11.75 -11.60

As can be seen from this table, the two step process delivered higher levels of POOA and POAA. It was also found that using the two step process described above generated lower temperatures than the one step process. These lower temperatures are important from both a safety and a stability standpoint for this reaction. Without wishing to be bound by any particular theory, it is thought that in the two step process, the kinetically slower perhydrolysis reaction of sorbitan octanoate was exposed to a more favorable perhydrolysis condition than in the one step reaction. That is in the two step process, the sorbitan octanoate is exposed to a higher pH and stoichiometrically more hydrogen peroxide. It is thought that these conditions contributed to the higher yield of POOA. Further, it is thought that the kinetically fast perhydrolysis reaction of triacetin was given enough perhydrolysis reaction time, but avoided a prolonged exposure to a high pH condition, and thus achieved a better POAA yield.

Example 3 –

A study was run to evaluate the ability to form a solid peroxycarboxylic acid forming composition. For this study, 2.5 grams of sorbitan octanoate was mixed with 2.5 grams of sodium bicarbonate in a beaker. Light sodium bicarbonate (2.5 grams) was then added. With stirring, the composition solidified quickly. Then, 2.5 grams of sodium percarbonate, and 1.04 grams of sodium hydroxide were added. The solid mixture was pressed in a mold with a 1.5 inch diameter, at a pressure of 2000 psi. A solid tablet was formed in one minute.

The solid was then added to 25 grams of deionized (DI) water, and stirred for 15 minutes. The solution was then sampled and measured for POOA concentration. The iodometric titration showed 1.08% POOA present in the solution. Thus, it was shown that a solid peroxycarboxylic acid forming composition can be generated in situ using an ester starting material.

Example 4 –

A study was run to evaluate the sanitizing efficacy of mixtures of peroxycarboxylic acids generated in situ from esters under alkaline conditions. For this study the following ester based peroxycarboxylic acid forming compositions were used.

Table 2.

Peroxyoctaonic Premix (POOA)		**Peroxyacetic Premix (POAA)**	
Composition	Amount (g)	Composition	Amount (g)
Sorbitan octanoate	2.50	Triacetin	4.90
35% Hydrogen Peroxide	2.26	35% Hydrogen Peroxide	10.58
Water	15.16	Water	42.31
10% NaOH	10.74	10% NaOH	42.21

The above Peroxycarboxylic acid premixes were then tested alone at various concentrations, and mixed at various concentrations against *Staphylococcus aureus* ATCC 6538, and *Escherichia coli* ATCC 11229. The pH was adjusted accordingly using nitric acid. The compositions tested are shown in the table below.

Table 3.

Test Substance	**Tested Concentration**	**Diluent**	**Test Solution (Volume of Test Substance/Total Volume)**	**pH**
POOA Premix	13 ppm	500 ppm Synthetic Hard Water (pH 7.80)	0.18g / 300 g	4.98
POAA Premix	61 ppm		0.64 g/ 300g	5.00
POOA + POAA	13 ppm + 61 ppm		0.32g + 1.07 g/ 500 g	4.99
POAA Premix	35 ppm		0.21 g/ 300 g	5.00
POOA Premix	15 ppm		0.37 g/ 300g	5.01
	20 ppm		0.45 g/ 300 g	4.98
POOA + POAA	20 ppm + 15 ppm		0.45g + 0.26 g/ 500 g	4.99
	15 ppm + 35 ppm		0.35g + 0.62 g/ 500g	5.01

The test substances were tested against *Staphylococcus aureus* ATCC 6538, and *Escherichia coli* ATCC 11229 at 25 °C ± 1°C for 30 seconds. A neutralizer screen was performed as part of the testing to verify that the neutralizer adequately neutralized the product and was not detrimental to the tested organisms. The inoculum numbers are shown in the table below.

Table 4.

Test System	**CFU/mL**	**Log_{10} Growth**	**Average Log_{10} growth**
Staphylococcus aureus ATCC 6538,	9.3×10^7	7.97	7.97
	9.5×10^7	7.98	
Escherichia coli ATCC 11229	1.10×10^8	8.04	8.05
	1.17×10^8	8.07	

The results from the various test substances are shown in the tables below.

Table 5.

***Staphylococcus aureus* ATCC 6538**				
Test Substance	**Exposure Time**	**Survivors (CFU/mL)**	**Average Log_{10} Survivors**	**Log Reduction**
13 ppm POOA + 61 ppm POAA	30 seconds	1.0×10^1, $< 1.0 \times 10^1$	1.00	6.97
20 ppm POOA + 15 ppm POAA	30 seconds	$<1.0 \times 10^1$, $<1.0 \times 10^1$	<1.00	>6.97
15 ppm POOA + 35 ppm POAA	30 seconds	$<1.0 \times 10^1$, $<1.0 \times 10^1$	<1.00	>6.97

Table 6.

***Escherichia coli* ATCC 11229**				
Test Substance	**Exposure Time**	**Survivors (CFU/mL)**	**Average Log_{10} Survivors**	**Log Reduction**
13 ppm POOA pH 4.98	30 seconds	4.22×10^7, 3.52×10^7	7.59	0.46
61 ppm POAA pH 5.00	30 seconds	3.0×10^3, 2.4×10^4	3.93	4.12
13 ppm POOA + 61 ppm POAA pH 4.99	30 seconds	$<1.0 \times 10^1$, $< 1.0 \times 10^1$	<1.00	>7.05
35 ppm POAA pH 5.00	30 seconds	1.85×10^7, 1.86×10^7	7.27	0.78
15 ppm POOA pH 5.01	30 seconds	1.06×10^7, 1.83×10^7	7.15	0.90
20 ppm POOA pH 4.98	30 seconds	7.0×10^5, 7.0×10^5	5.85	2.20
20 ppm POOA + 15 ppm POAA	30 seconds	$<1.0 \times 10^1$, $<1.0 \times 10^1$	<1.00	>7.05
15 ppm POOA + 35 ppm POAA	30 seconds	$<1.0 \times 10^1$, $<1.0 \times 10^1$	<1.00	>7.05

As can be seen from these results, at every concentration tested, POOA and POAA alone at pH 5.0 failed the sanitizer test with less than 5 log reductions of *Escherichia coli* after 30 seconds. A passing result for a sanitizing efficacy screen requires a greater than 5 log reduction in test system growth after a 30 second exposure time. However, a synergistic effect was observed between POOA and POAA when mixed together. For example a complete kill of both *Staphylococcus aureus and Escherichia coli* was observed after a 30 second exposure time with the mixed systems.

Example 5 –

A study was run to evaluate the ability to form peroxycarboxylic acids from ester starting materials in various solvents. First, a test was run to determine the ability to form a peroxycarboxylic acid (POOA) from glyceryl trioctanoate using water as the solvent. For this test, 2.50 grams of glyceryl trioctanoate was added to 2.25 grams of 35% hydrogen peroxide. Then, 30 grams of deionized water, and 10.50 grams of a 10% aqueous sodium hydroxide solution were added. All of these components were added in serial fashion to a 150 mL Pyrex beaker fitted with a magnetic stir bar. Just prior to the addition of the sodium hydroxide, stirring was initiated and maintained through all of the subsequent addition steps. Samples of the reaction solution were taken at 15, 27, and 40 minutes. The samples were treated with acetic acid, and titrated using an iodometric peroxycarboxylic acid titration to measure the peroxycarboxylic acid concentration. The results are shown in Table 7.

A comparative example was then run using a semi-methanolic reaction solution. For this comparative example, 2.50 grams of glyceryl trioctanoate was added to 2.25 grams of 35% hydrogen peroxide followed by 30 grams of 100% methanol, and 10.50 grams of a

10% aqueous sodium hydroxide solution. All of these components were added in serial fashion to a 150 mL Pyrex beaker fitted with a magnetic stir bar. Just prior to the addition of the sodium hydroxide, stirring was initiated and maintained through all of the subsequent steps. Samples of the reaction solution were taken at 10, 20, and 30 minutes and treated with acetic acid and titrated using a standard iodometric peroxycarboxylic acid titration. The results from this semi-methanolic reaction solution comparative example are also shown in Table 7.

Finally, another comparative example was run using a purely alcoholic reaction solution. For this comparative example, 2.50 grams of glyceryl trioctanoate was added to 6.75 grams of 10% urea-hydrogen peroxide-ethanol solution followed by 30 grams of 100% methanol, and 14.70 grams of a 10% potassium hydroxide/methanol solution. All of these components were added in serial fashion to a 150 mL Pyrex beaker fitted with a magnetic stir bar. Just prior to the addition of the potassium hydroxide solution, stirring was initiated and maintained through all of the subsequent steps. Samples of the reaction solution were taken at 8, 26, 47, and 69 minutes. The samples were treated with acetic acid, and titrated using a standard iodometric peroxycarboxylic acid titration to measure for peroxycarboxylic acid concentration. The results are also shown in Table 7 below.

Table 7.

	Purely Aqueous Reaction Solution		**Semi-Methanolic Reaction Solution**		**Pure Methanolic Reaction Solution**	
Reaction Time (min)	POOA (%)	Portion Converted (%)	POOA (%)	Portion Converted (%)	POOA (%)	Portion Converted (%)
8					1.59	34.0
10			1.00	18.0		
15	0.00	0.00				
20			1.89	34.0		
26					1.69	36.1

27	0.00	0.00				
30			2.32	42.0		
40	0.00	0.00				
47					1.59	34.0
69					1.59	34.0

As can be seen from this table, in a purely aqueous reaction, no POOA was formed. Without wishing to be bound by any particular theory, it is thought that the HLB of glyceryl trioctanoate is too low (less than 3). That is, the low water solubility/dispersability of glyceryl trioctanoate prohibits the perhydrolysis reaction in the purely aqueous environment, regardless of the otherwise favorable perhydrolysis conditions. This surprising result is true for sugar esters in general with an HLB less than 3. For example, sorbitan trioctanoate (HLB less than 3) could not be perhydrolized in an aqueous solution to generate peroxyoctanoic acid, however, sorbitan monooctanoate (HLB greater than 3) was readily perhydrolysibile in aqueous solutions.

CLAIMS

1. A peroxycarboxylic acid forming composition comprising:

an ester of a polyhydric alcohol and a C1 to C18 carboxylic acid;

a source of alkalinity; and

an oxidizing agent;

wherein said composition is not at equilibrium, has a pH greater than about 12, and is substantially free of a stabilizing agent, and a surfactant.

2. The composition of claim 1, wherein the carboxylic acid comprises a C5 to C11 carboxylic acid.

3. The composition of claim 1, wherein the polyhydric alcohol is selected from the group consisting of a sugar, a sugar alcohol, and mixtures and derivatives thereof.

4. The composition of claim 3, wherein the sugar comprises sucrose.

5. The composition of claim 3, wherein the sugar alcohol is selected from the group consisting of ethylene glycol, propylene glycol, glycerol, polyglycerol, sorbitol, sorbitan, and mixtures and derivatives thereof.

6. The composition of claim 1, wherein the ester is selected from the group consisting of monooctanoic glyceride, dioctanoic glyceride, trioctaonoic glyceride, sorbitan

monooctanoate, sorbitan dioctanoate, sorbitan trioctanoate, sorbitan tetraoctanoate, laurate sucroside, monoacetin, diacetin, triacetin and mixtures and derivatives thereof.

7. The composition of claim 1, wherein the oxidizing agent comprises a hydrogen peroxide donor.

8. The composition of claim 1, wherein the oxidizing agent comprises a peroxide source selected from the group consisting of a percarbonate, a perborate urea hydrogen peroxide, PVP-peroxides and mixtures thereof.

9. The composition of claim 1, wherein the source of alkalinity is selected from the group consisting of an alkaline metal hydroxide, an alkaline earth metal hydroxide, an alkali metal silicate, an alkali metal carbonate, borates and mixtures thereof.

10. The composition of claim 1, further comprising a solvent.

11. The composition of claim 10, wherein the solvent is selected from the group consisting of water, an alcohol, and mixtures thereof.

12. The composition of claim 10, wherein the solvent is water and the HLB of the ester is greater than about 3.

13. The composition of claim 1, wherein the composition comprises:

about 0.01 wt% to about 95 wt% of the ester;

about 0.001 wt% to about 25 wt% of the source of alkalinity; and

about 0.001 wt% to about 50 wt% of the oxidizing agent.

14. The composition of claim 13, further comprising about 10 wt% to about 99 wt% of a solvent.

15. The composition of claim 1, wherein the composition is substantially free of a surfactant.

16 The composition of claim 1, wherein the pH is greater than about 12.5.

17. A mixed peroxycarboxylic acid forming composition comprising:

(a) about 0.01 wt% to about 95wt% of a first ester of a polyhydric alcohol and a C1 to C18 carboxylic acid;

(b) about 0.01 wt% to about 95wt% of a second ester of a polyhydric alcohol and a C1 to C18 carboxylic acid;

(c) about 0.001 wt% to about 25 wt% of a source of alkalinity; and

(d) about 0.001 wt% to about 50 wt% of an oxidizing agent, wherein the first and second esters are not the same, the composition is not at equilibrium, and the composition is substantially free of a stabilizing agent.

18. The composition of claim 17, wherein the first ester comprises a C1 to C4 carboxylic acid ester, and the second ester comprises a C5 to C11 carboxylic acid ester.

19. The composition of claim 18, wherein the first ester comprises triacetin and the second ester comprises sorbitan octanoate.

20. The composition of claim 17, wherein the oxidizing agent comprises hydrogen peroxide donor.

21. The composition of claim 17, wherein the oxidizing agent comprises a peroxide source selected from the group consisting of a percarbonate, a perborate, urea hydrogen peroxide, PVP-peroxides and mixtures thereof.

22. The composition of claim 17, wherein the source of alkalinity is selected from the group consisting of an alkaline metal hydroxide, an alkaline earth metal hydroxide, an alkali metal silicate, an alkali metal carbonate and mixtures thereof.

23. The composition of claim 17, further comprising a solvent.

24. The composition of claim 23, wherein the solvent is selected from the group consisting of water, an alcohol, and mixtures thereof.

25. The composition of claim 16, wherein the composition comprises:

about 0.01 wt% to about 95 wt% of the ester;

about 0.001 wt% to about 25 wt% of the source of alkalinity; and

about 0.001 wt% to about 50 wt% of an oxidizing agent.

26. The composition of claim 24, further comprising about 10 wt% to about 99 wt% of a solvent.

27. The composition of claim 17, wherein the composition is substantially free of a surfactant.

28. A method for forming a disinfecting composition, said method comprising:

(a) providing a mixed peroxycarboxylic acid composition comprising:

(i) a first ester of a polyhydric alcohol and a C1 to C18 carboxylic acid ;

(ii) a second ester of a polyhydric alcohol and a C1 to C18 carboxylic acid;

(iii) a source of alkalinity; and

(iv) an oxidizing agent;

(b) providing an acidic aqueous solution;

(c) diluting the mixed peroxycarboxylic acid composition with the acidic aqueous solution to a pH of about 1.0 to about 8.0 to form the disinfecting composition.

29. A method for disinfecting a surface comprising contacting the surface with a mixed peroxycarboxylic acid disinfecting composition formed by diluting a composition

comprising a first ester of a polyhydric alcohol and a C1 to C18 carboxylic acid, a second ester of a polyhydric alcohol and a C1 to C18 carboxylic acid, a source of alkalinity, and an oxidizing agent, with an aqueous acidic solution to a pH of about 1 to about 8.

30. A method for forming a disinfecting composition, said method comprising:

(a) providing a peroxycarboxylic acid composition comprising:

(i) an ester of a polyhydric alcohol and a C1 to C18 carboxylic acid;

(ii) a source of alkalinity; and

(iii) an oxidizing agent; wherein said composition has a pH greater than 12;

(b) providing an acidic aqueous solution;

(c) diluting the peroxycarboxylic acid composition with the acidic aqueous solution to a pH of about 1.0 to about 8.0 to form the disinfecting composition.

31. A method for forming a percarboxylic acid composition comprising

(a) providing a reaction mixture comprising:

(i) an ester of a polyhydric alcohol and a C1 to C18 carboxylic acid;

(ii) a source of alkalinity; and

(iii) an oxidizing agent, wherein the reaction mixture has a pH greater than about 12;

(b) allowing the reaction mixture to react for a sufficient amount of time such that a C1 to C18 percarboxylic acid is formed.

32. The method of claim 31, wherein the pH is greater than about 12.5.

33. A method for forming a mixed percarboxylic acid composition comprising

(a) providing a reaction mixture comprising:

(i) a first ester of a polyhydric alcohol and a C1 to C18 carboxylic acid;

(ii) a source of alkalinity; and

(iii) an oxidizing agent;

(b) allowing the reaction mixture to react for a sufficient amount of time, and then adding a second ester of a polyhydric alcohol and a C1 to C18, and

(c) after addition of the second ester allowing the mixture to react for a sufficient amount of time such that a mixed peroxycarboxylic acid composition is formed.

ABSTRACT

The present disclosure is related to percarboxylic acid compositions formed in situ in non-equilibrium reactions. The peroxycarboxylic acid compositions are formed using ester based starting materials. Methods for using the percarboxylic acid compositions are also disclosed.

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(12) **United States Patent**
Li et al.

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(45) **Date of Patent: *Nov. 4, 2014**

(54) **IN SITU GENERATION OF PEROXYCARBOXYLIC ACIDS AT ALKALINE PH, AND METHODS OF USE THEREOF**

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(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

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C07C 69/30	(2006.01)
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USPC **424/616**; 562/2; 562/3; 562/4; 562/6; 422/28; 568/568

(58) **Field of Classification Search**

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See application file for complete search history.

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Assistant Examiner — Irina Neagu
(74) *Attorney, Agent, or Firm* — McKee, Voorhees & Sease

(57) **ABSTRACT**

The present disclosure is related to percarboxylic acid compositions formed in situ in non-equilibrium reactions. The peroxycarboxylic acid compositions are formed using ester based starting materials. Methods for using the percarboxylic acid compositions are also disclosed.

22 Claims, 6 Drawing Sheets

EXHIBIT H

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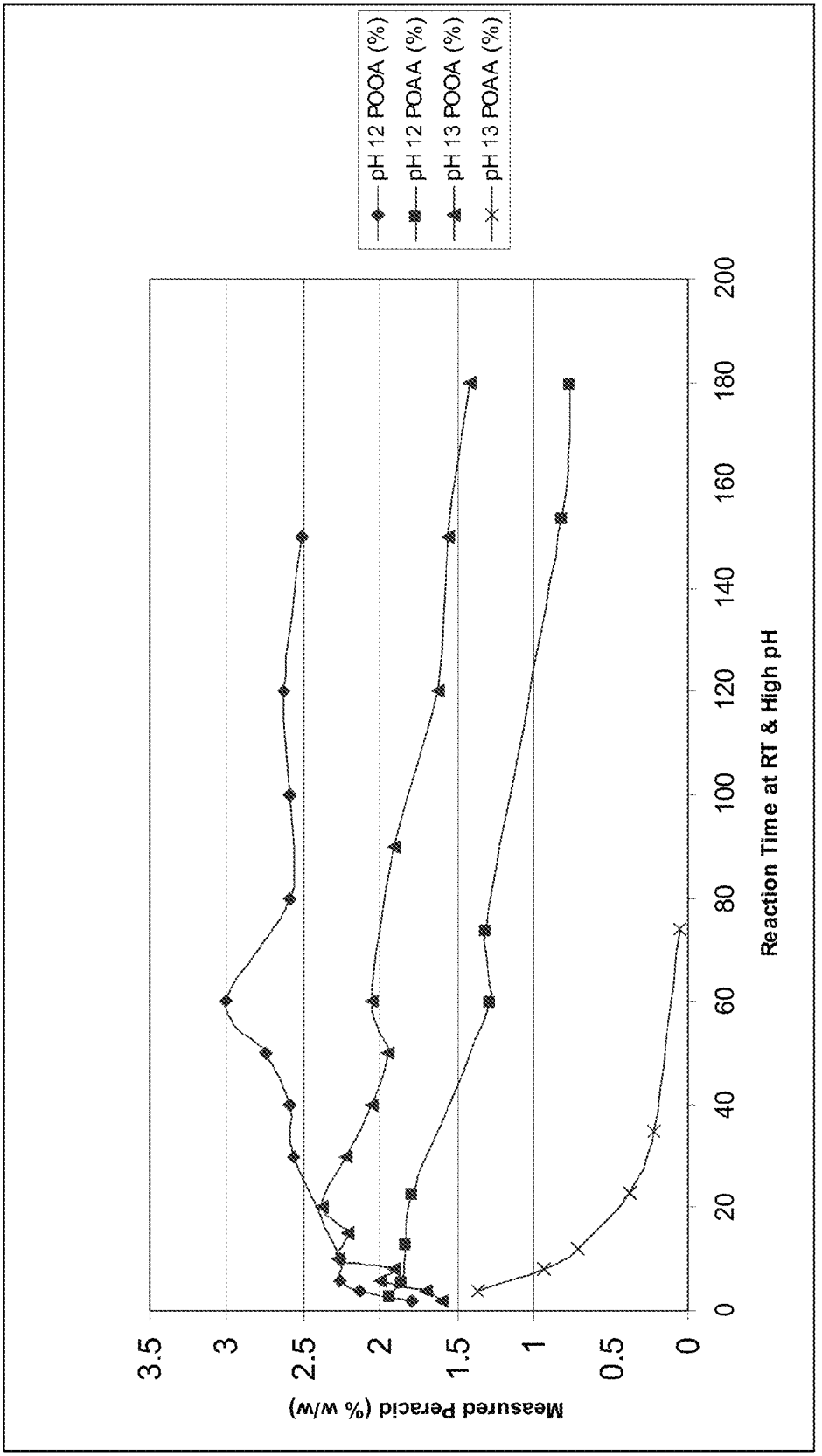

pH 12 POOA (%)
pH 12 POAA (%)
pH 13 POOA (%)
pH 13 POAA (%)
Measured Peracid (% w/w)
0
0.5
1
1.5
2
2.5
3
3.5
Reaction Time at RT & High pH
0
20
40
60
80
100
120
140
160
180
200

FIG. 1

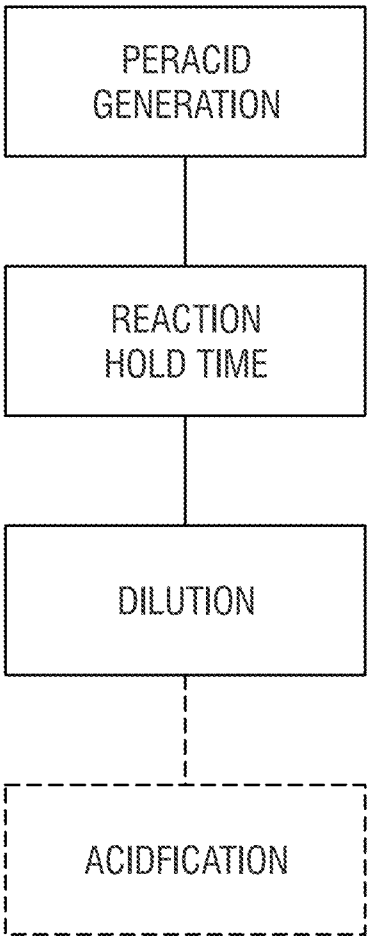

PERACID GENERATION
REACTION HOLD TIME
DILUTION
ACIDFICATION

FIG. 2

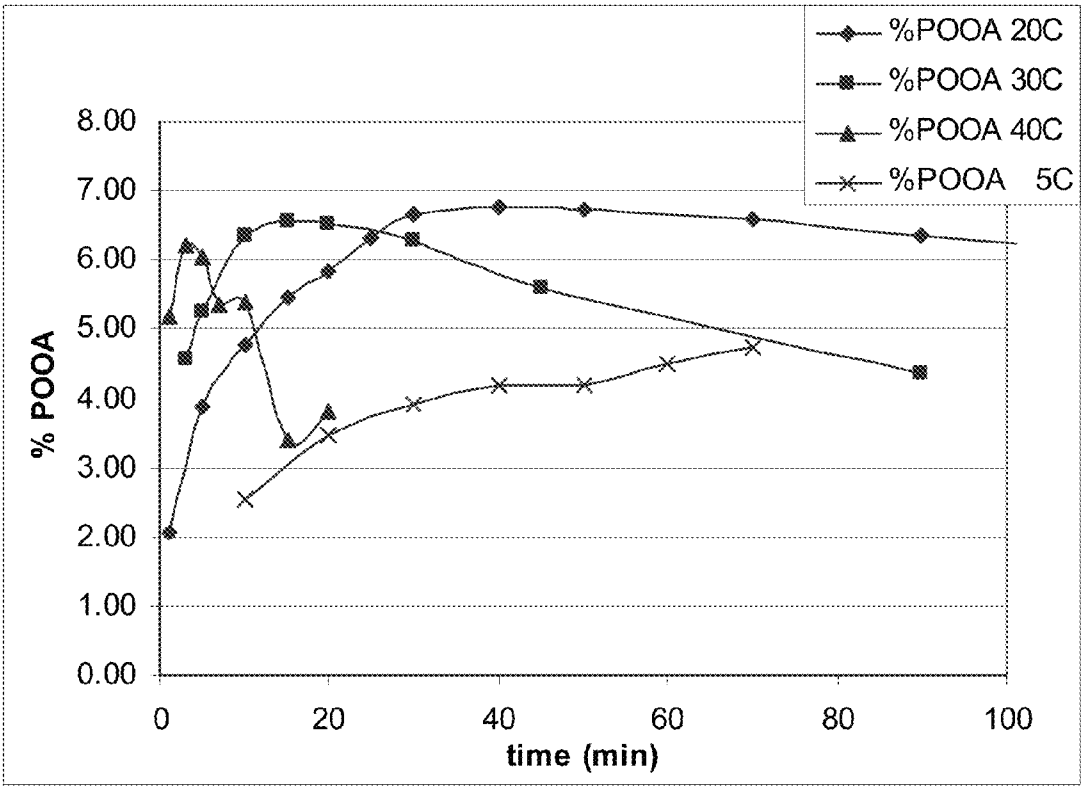

%POOA 20C
%POOA 30C
%POOA 40C
%POOA 5C
8.00
7.00
6.00
5.00
4.00
3.00
2.00
1.00
0.00
% POOA
0
20
40
60
80
100
time (min)

FIG. 3

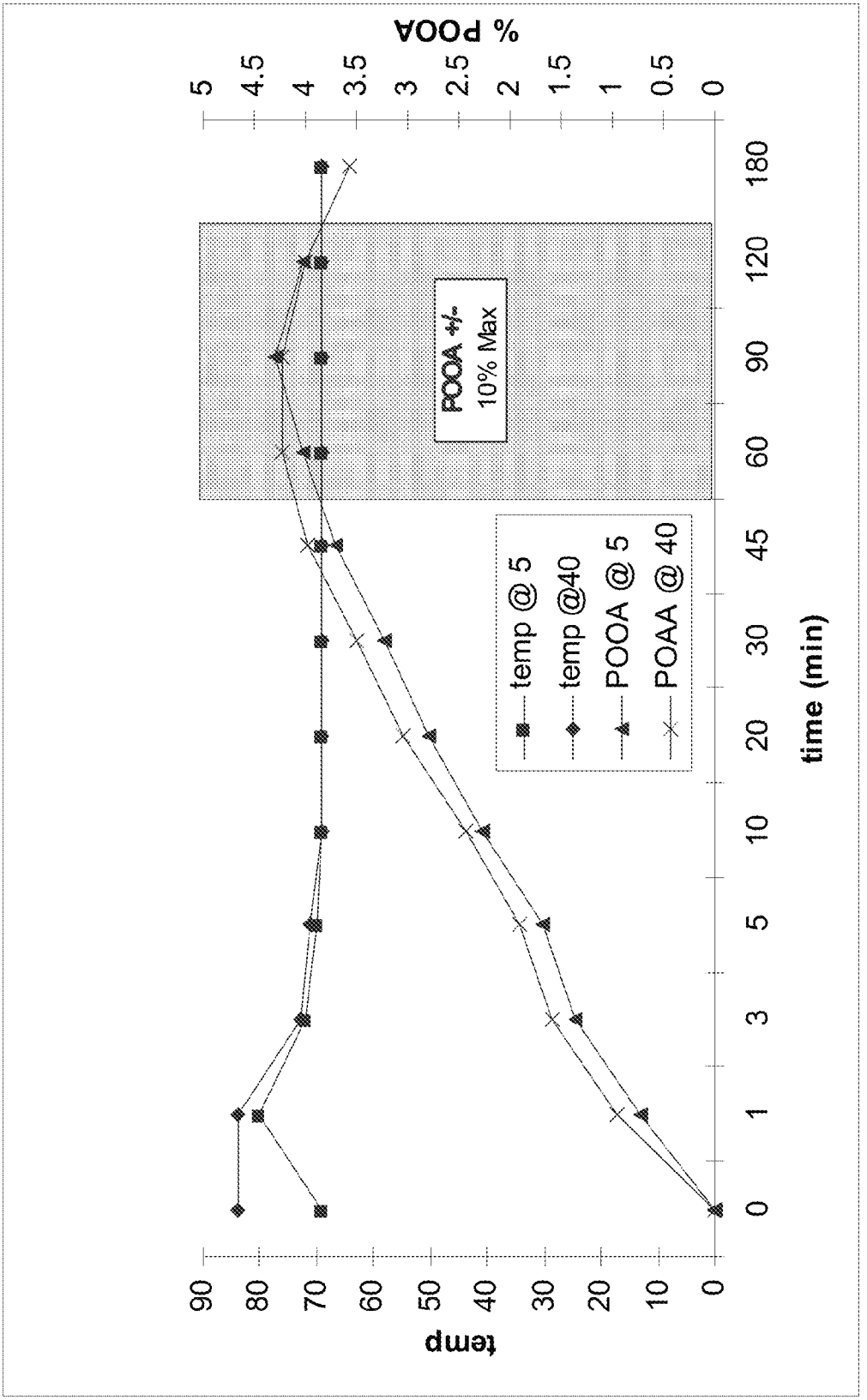

POOA %
5
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
180
120
90
60
45
30
20
10
5
3
1
0
time (min)
POOA +/-
10% Max
temp @ 5
temp @40
POOA @ 5
POAA @ 40
temp
90
80
70
60
50
40
30
20
10
0

FIG. 4

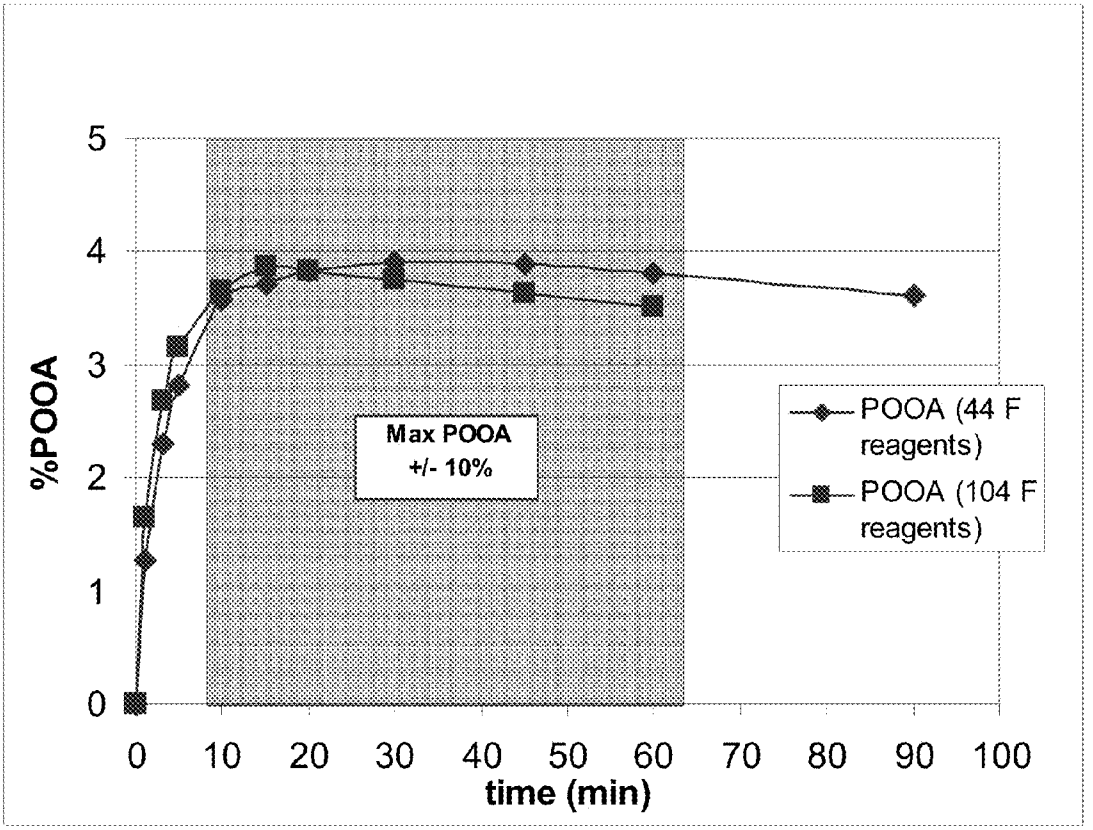

%POOA
time (min)
Max POOA
+/- 10%
POOA (44 F reagents)
POOA (104 F reagents)
0
1
2
3
4
5
0
10
20
30
40
50
60
70
80
90
100

FIG. 5

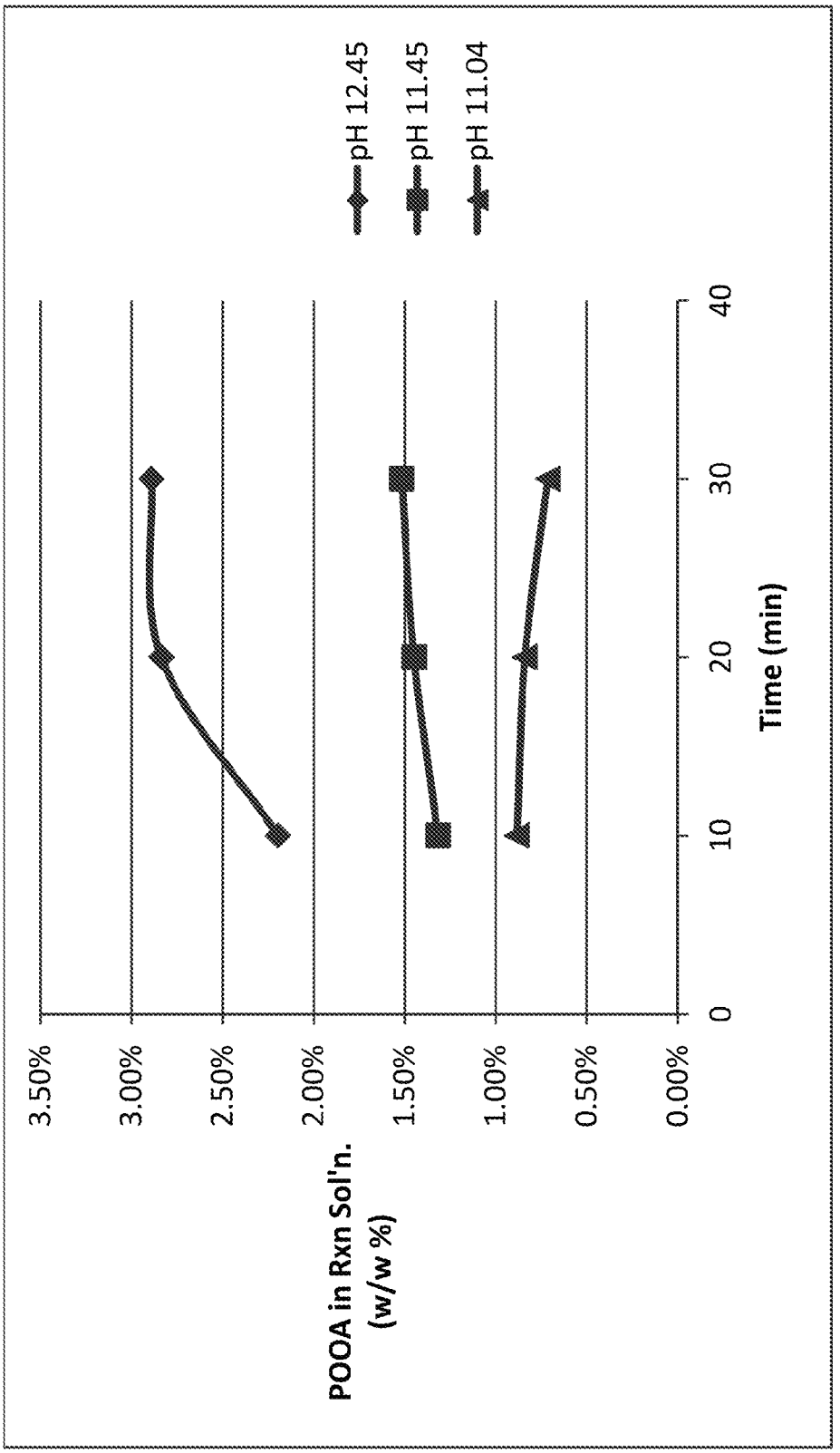

pH 12.45
pH 11.45
pH 11.04
3.50%
3.00%
2.50%
2.00%
1.50%
1.00%
0.50%
0.00%
POOA in Rxn Sol'n. (w/w %)
0
10
20
30
40
Time (min)

FIG. 6

IN SITU GENERATION OF PEROXYCARBOXYLIC ACIDS AT ALKALINE PH, AND METHODS OF USE THEREOF

CROSS REFERENCE TO RELATED APPLICATIONS

This application is a nonprovisional application of U.S. Provisional Application No. 61/427,965, filed Dec. 29, 2010, entitled In Situ Generation of Peroxycarboxylic Acids at Alkaline pH and Methods of Use Thereof, which is herein incorporated by reference in its entirety.

This application is related to U.S. patent application Ser. No. 13/331,304, entitled In Situ Generation of Peroxycarboxylic Acids at Alkaline pH and Methods of Use Thereof, U.S. patent application Ser. Nos. 61/427,951 and 13/330,915, entitled Sugar Ester Peracid On-Site Generator and Formulator, U.S. patent application Ser. No. 13/330,981, entitled Continuous On-Line Adjustable Disinfectant/Sanitizer/Bleach Generator, U.S. patent application Ser. No. 13/331,104, entitled Generation of Peroxycarboxylic Acids at Alkaline pH, and Their Use as Textile Bleaching and Antimicrobial Agents, and U.S. patent application Ser. No. 13/331,385, entitled Water Temperature as a Means of Controlling Kinetics of Onsite Generated Peracids, each filed concurrently herewith. The entire contents of these patent applications are hereby expressly incorporated herein by reference including, without limitation, the specification, claims and abstract, as well as any figures, tables or drawings thereof.

FIELD OF THE INVENTION

The present disclosure relates to compositions and methods for the in situ generation of peroxycarboxylic acid compositions, at alkaline pH levels, viz. greater than about pH 12. The present disclosure also relates to methods for the in situ generation of mixed percarboxylic acid compositions, and methods of using the in situ generated peroxycarboxylic acid compositions.

BACKGROUND OF THE INVENTION

Peroxycarboxylic acids are known for use as antimicrobials and bleaching agents. Mixed peroxycarboxylic acid systems are also known for use as antimicrobial and bleaching agents. However, there are disadvantages to use of these antimicrobial and bleaching agents. For example, the most commonly used peroxycarboxylic acid, peroxyacetic acid, is known to have a strong pungent odor. In addition, peracids such as peroxycarboxylic acid have known chemical disadvantages, namely, they are relatively unstable in solution and decompose to the corresponding carboxylic acids and oxygen.

Conventional peroxycarboxylic acid compositions are made through an acid catalyzed equilibrium reaction. Most often, the peroxycarboxylic acids are generated in a chemical plant, and then shipped to customers for on-site use. Due to the limited storage stability of peroxycarboxylic acids, the peroxycarboxylic acids must be packed in special containers and shipped under the strict Department of Transportation (DOT) guidelines. Certain improvements to peroxycarboxylic acid stability have proved advantageous for shipping purposes, as described in U.S. patent application Ser. No. 11/847,604, entitled "Shelf Stable, Reduced Corrosion, Ready to Use Peroxycarboxylic Acid Antimicrobial Compositions," the entire contents of which are hereby expressly incorporated herein by reference. Most commercially available products in an equilibrium mixture contain excess hydrogen peroxide in the presence of stabilizers and acid catalysts, to stabilize and improve the composition's shelf life. Despite such stability improvements, excess amounts of reagents (e.g., acids, oxidizing agents, and stabilizers) are present in the compositions during shipping to prevent decomposition. These and other disadvantages to the use of peracid compositions exist.

Accordingly, it is an objective of the claimed invention to develop in situ methods for generation of peroxycarboxylic acids at alkaline pH.

A further object of the invention is an in situ method for generation of stable single peracid systems that are substantially free of stabilizing agents and/or surfactants.

A further object of the invention is an in situ method for generation of stable mixed peracid systems that are substantially free of stabilizing agents and/or surfactants.

A still further object of the invention is to develop concentrated peracid chemistries for further dilution and/or use on site within a matter of hours to days in order to eliminate the need for various stabilizing agents in the compositions to ensure storage stability (e.g. stability for at least one year as required for regulated chemistries).

BRIEF SUMMARY OF THE INVENTION

In some aspects, the present disclosure relates to peroxycarboxylic acid forming compositions. The compositions comprise a first reagent premix comprising at least one ester of a polyhydric alcohol and a C1 to C18 carboxylic acid, and one or more agents selected from the group consisting of an oxidizing agent, a dispersing agent, a solvent, water and mixtures thereof; wherein the solvent is an organic solvent to solubilize the ester; wherein the dispersing agent is sufficient to create a physically meta-stable solution upon reaction with a source of alkalinity and the subsequent acidification; and a second reagent source comprising the source of alkalinity; wherein said composition is not at equilibrium, has a pH greater than about 12, and is substantially free of a stabilizing agent.

In other aspects, the present disclosure relates a peroxycarboxylic acid forming composition comprising a first reagent premix comprising at least one ester of a polyhydric alcohol and a C1 to C18 carboxylic acid, an oxidizing agent and a dispersing agent; wherein the dispersing agent is sufficient to create a physically meta-stable solution upon reaction with a source of alkalinity and the subsequent acidification; and a second reagent source comprising a source of alkalinity; wherein said composition is not at equilibrium, has a pH greater than about 12, and is substantially free of a stabilizing agent.

In other aspects, the present disclosure relates to methods for delivering an antimicrobial comprising contacting the surface with an antimicrobial composition formed by diluting a composition first reagent premix comprising at least one ester of a polyhydric alcohol and a C1 to C18 carboxylic acid, an oxidizing agent and a dispersing agent, and a second reagent source comprising a source of alkalinity, with an aqueous acidic solution to a pH of about 1 to about 8, wherein the solvent is an organic solvent to solubilize the ester; and wherein the dispersing agent is sufficient to create a physically meta-stable solution upon reaction with a source of alkalinity.

In other aspects, the present disclosure provides a method for forming an antimicrobial composition, comprising: (a) providing a peroxycarboxylic acid composition having active peroxycarboxylic acid content from about 0.25% to about 20% comprising: (i) a first reagent premix comprising at least

one ester of a polyhydric alcohol and a C1 to C18 carboxylic acid, and one or more agents selected from the group consisting of an oxidizing agent, a dispersing agent, a solvent, water and mixtures thereof; wherein the solvent is an organic solvent to solubilize the ester; wherein the dispersing agent is sufficient to create a physically meta-stable solution upon reaction with a source of alkalinity; and (ii) a second reagent source comprising a source of alkalinity; wherein said composition has a pH greater than 12 and is not at equilibrium; (b) diluting the peroxycarboxylic acid composition to an alkaline solution having an active peroxycarboxylic acid content from about 0.01% to about 1%; (c) providing an acidic aqueous solution; and (d) diluting the peroxycarboxylic acid composition with the acidic aqueous solution to a pH of about 1.0 to about 8.0 to form the antimicrobial composition.

In still yet other aspects, the present disclosure provides methods for forming an antimicrobial composition comprising: (a) providing a peroxycarboxylic acid composition having active peroxycarboxylic acid content from about 0.25% to about 20% comprising: (i) a first reagent premix comprising at least one ester of a polyhydric alcohol and a C1 to C18 carboxylic acid, and one or more agents selected from the group consisting of an oxidizing agent, a dispersing agent, a solvent, water and mixtures thereof; wherein the dispersing agent is sufficient to create a physically meta-stable solution upon reaction with a source of alkalinity; and (ii) a second reagent source comprising a source of alkalinity; wherein said composition has a pH greater than 12 and is not at equilibrium; (b) allowing the peroxycarboxylic acid composition to react for a sufficient amount of time such that a C1 to C18 percarboxylic acid is formed to generate an antimicrobial composition; and (c) providing said composition to an application for use without an acidification step.

While multiple embodiments are disclosed, still other embodiments of the present invention will become apparent to those skilled in the art from the following detailed description, which shows and describes illustrative embodiments of the invention. Accordingly, the drawings and detailed description are to be regarded as illustrative in nature and not restrictive.

BRIEF DESCRIPTION OF DRAWINGS

FIG. **1** is a graphical depiction of the stability of various peroxycarboxylic acid compositions formed from esters at an alkaline pH over time.

FIG. **2** shows a diagram of an embodiment of methods of making the peracid chemistry according to the invention.

FIG. **3** shows a graph representing POOA concentration over time at various reaction temperatures according to various embodiments of the invention.

FIG. **4** shows a graph representing POOA production at various temperatures over a period of time according to various embodiments of the invention.

FIG. **5** shows a graph representing POOA production and temperature as a function of time according to various embodiments of the invention.

FIG. **6** shows a graph of peracid generated in a reaction solution according to the invention at varying pH.

Various embodiments of the present invention will be described in detail with reference to the drawings, wherein like reference numerals represent like parts throughout the several views. Reference to various embodiments does not limit the scope of the invention. Figures represented herein are not limitations to the various embodiments according to the invention and are presented for exemplary illustration of the invention.

DETAILED DESCRIPTION OF THE INVENTION

The present disclosure relates to peroxycarboxylic acid compositions generated in situ from a non-equilibrium ester based reaction, as well as methods of making and using such compositions. The compositions disclosed herein have many advantages over conventional, equilibrium based peroxycarboxylic acid compositions. For example, after peroxycarboxylic acid formation according to methods disclosed herein, the compositions have significantly lower levels of reactant residues compared to peroxycarboxylic acid compositions generated using equilibrium reactions. Further, as the compositions are generated in situ, and can be generated on site, the compositions can be substantially free of, or even free of, stabilizers. Additionally, due to the ability to generate the disclosed peroxycarboxylic acid compositions on site, the step of shipping hazardous peroxycarboxylic acid compositions to an end user can be eliminated. This beneficially allows a user to provide diluted compositions for a particular application without having to ship large amounts of a diluted composition. These and other benefits of the present invention are disclosed herein.

The embodiments of this invention are not limited to particular peroxycarboxylic acid compositions and methods for in situ generation of the same, which can vary and are understood by skilled artisans. It is further to be understood that all terminology used herein is for the purpose of describing particular embodiments only, and is not intended to be limiting in any manner or scope. For example, as used in this specification and the appended claims, the singular forms "a," "an" and "the" can include plural referents unless the content clearly indicates otherwise. Further, all units, prefixes, and symbols may be denoted in its SI accepted form. Numeric ranges recited within the specification are inclusive of the numbers defining the range and include each integer within the defined range.

So that the present invention may be more readily understood, certain terms are first defined. Unless defined otherwise, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which embodiments of the invention pertain. Many methods and materials similar, modified, or equivalent to those described herein can be used in the practice of the embodiments of the present invention without undue experimentation, the preferred materials and methods are described herein. In describing and claiming the embodiments of the present invention, the following terminology will be used in accordance with the definitions set out below.

As used herein, the term "about" refers to variation in the numerical quantity that can occur, for example, through typical measuring and liquid handling procedures used for making concentrates or use solutions in the real world; through inadvertent error in these procedures; through differences in the manufacture, source, or purity of the ingredients used to make the compositions or carry out the methods; and the like. The term "about" also encompasses amounts that differ due to different equilibrium conditions for a composition resulting from a particular initial mixture. Whether or not modified by the term "about", the claims include equivalents to the quantities.

As used herein, the phrase "air streams" includes food anti-spoilage air circulation systems. Air streams also include

air streams typically encountered in hospital, surgical, infirmity, birthing, mortuary, and clinical diagnosis rooms.

As used herein, "agricultural" or "veterinary" objects or surfaces include animal feeds, animal watering stations and enclosures, animal quarters, animal veterinarian clinics (e.g. surgical or treatment areas), animal surgical areas, and the like.

As used herein, the term "alkyl" or "alkyl groups" refers to saturated hydrocarbons having one or more carbon atoms, including straight-chain alkyl groups (e.g., methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, etc.), cyclic alkyl groups (or "cycloalkyl" or "alicyclic" or "carbocyclic" groups) (e.g., cyclopropyl, cyclopentyl, cyclohexyl, cycloheptyl, cyclooctyl, etc.), branched-chain alkyl groups (e.g., isopropyl, tert-butyl, sec-butyl, isobutyl, etc.), and alkyl-substituted alkyl groups (e.g., alkyl-substituted cycloalkyl groups and cycloalkyl-substituted alkyl groups).

Unless otherwise specified, the term "alkyl" includes both "unsubstituted alkyls" and "substituted alkyls." As used herein, the term "substituted alkyls" refers to alkyl groups having substituents replacing one or more hydrogens on one or more carbons of the hydrocarbon backbone. Such substituents may include, for example, alkenyl, alkynyl, halogeno, hydroxyl, alkylcarbonyloxy, arylcarbonyloxy, alkoxycarbonyloxy, aryloxy, aryloxycarbonyloxy, carboxylate, alkylcarbonyl, arylcarbonyl, alkoxycarbonyl, aminocarbonyl, alkylaminocarbonyl, dialkylaminocarbonyl, alkylthiocarbonyl, alkoxyl, phosphate, phosphonato, phosphinato, cyano, amino (including alkyl amino, dialkylamino, arylamino, diarylamino, and alkylarylamino), acylamino (including alkylcarbonylamino, arylcarbonylamino, carbamoyl and ureido), imino, sulfhydryl, alkylthio, arylthio, thiocarboxylate, sulfates, alkylsulfinyl, sulfonates, sulfamoyl, sulfonamido, nitro, trifluoromethyl, cyano, azido, heterocyclic, alkylaryl, or aromatic (including heteroaromatic) groups.

In some embodiments, substituted alkyls can include a heterocyclic group. As used herein, the term "heterocyclic group" includes closed ring structures analogous to carbocyclic groups in which one or more of the carbon atoms in the ring is an element other than carbon, for example, nitrogen, sulfur or oxygen. Heterocyclic groups may be saturated or unsaturated. Exemplary heterocyclic groups include, but are not limited to, aziridine, ethylene oxide (epoxides, oxiranes), thiirane (episulfides), dioxirane, azetidine, oxetane, thietane, dioxetane, dithietane, dithiete, azolidine, pyrrolidine, pyrroline, oxolane, dihydrofuran, and furan.

The term "cleaning," as used herein, means to perform or aid in soil removal, bleaching, microbial population reduction, or combination thereof.

For the purpose of this patent application, successful microbial reduction is achieved when the microbial populations are reduced by at least about 50%, or by significantly more than is achieved by a wash with water. Larger reductions in microbial population provide greater levels of protection.

As used herein, the term "disinfectant" refers to an agent that kills all vegetative cells including most recognized pathogenic microorganisms, using the procedure described in *A.O.A.C. Use Dilution Methods*, Official Methods of Analysis of the Association of Official Analytical Chemists, paragraph 955.14 and applicable sections, 15th Edition, 1990 (EPA Guideline 91-2). As used herein, the term "high level disinfection" or "high level disinfectant" refers to a compound or composition that kills substantially all organisms, except high levels of bacterial spores, and is effected with a chemical germicide cleared for marketing as a sterilant by the Food and Drug Administration. As used herein, the term "intermediate-level disinfection" or "intermediate level disinfectant" refers to a compound or composition that kills mycobacteria, most viruses, and bacteria with a chemical germicide registered as a tuberculocide by the Environmental Protection Agency (EPA). As used herein, the term "low-level disinfection" or "low level disinfectant" refers to a compound or composition that kills some viruses and bacteria with a chemical germicide registered as a hospital disinfectant by the EPA.

As used herein, the phrase "food processing surface" refers to a surface of a tool, a machine, equipment, a structure, a building, or the like that is employed as part of a food processing, preparation, or storage activity. Examples of food processing surfaces include surfaces of food processing or preparation equipment (e.g., slicing, canning, or transport equipment, including flumes), of food processing wares (e.g., utensils, dishware, wash ware, and bar glasses), and of floors, walls, or fixtures of structures in which food processing occurs. Food processing surfaces are found and employed in food anti-spoilage air circulation systems, aseptic packaging sanitizing, food refrigeration and cooler cleaners and sanitizers, ware washing sanitizing, blancher cleaning and sanitizing, food packaging materials, cutting board additives, third-sink sanitizing, beverage chillers and warmers, meat chilling or scalding waters, auto dish sanitizers, sanitizing gels, cooling towers, food processing antimicrobial garment sprays, and non-to-low-aqueous food preparation lubricants, oils, and rinse additives.

As used herein, the phrase "food product" includes any food substance that might require treatment with an antimicrobial agent or composition and that is edible with or without further preparation. Food products include meat (e.g. red meat and pork), seafood, poultry, produce (e.g., fruits and vegetables), eggs, living eggs, egg products, ready to eat food, wheat, seeds, roots, tubers, leafs, stems, corns, flowers, sprouts, seasonings, or a combination thereof. The term "produce" refers to food products such as fruits and vegetables and plants or plant-derived materials that are typically sold uncooked and, often, unpackaged, and that can sometimes be eaten raw.

As used herein, the term "fouling" shall be understood to mean the undesirable presence of or any deposition of any organic or inorganic material in the applicable composition or chemistry.

As used herein, the term "free" or "substantially free" refers to a composition, mixture, or ingredient that does not contain a particular compound or to which a particular compound or a particular compound-containing compound has not been added. Should the particular compound be present through contamination and/or use in a minimal amount of a composition, mixture, or ingredients, the amount of the compound shall be less than about 3 wt-%. More preferably, the amount of the compound is less than 2 wt-%, less than 1 wt-%, and most preferably the amount of the compound is less than 0.5 wt-%.

As used herein, the phrase "health care surface" refers to a surface of an instrument, a device, a cart, a cage, furniture, a structure, a building, or the like that is employed as part of a health care activity. Examples of health care surfaces include surfaces of medical or dental instruments, of medical or dental devices, of electronic apparatus employed for monitoring patient health, and of floors, walls, or fixtures of structures in which health care occurs. Health care surfaces are found in hospital, surgical, infirmity, birthing, mortuary, and clinical diagnosis rooms. These surfaces can be those typified as "hard surfaces" (such as walls, floors, bed-pans, etc.), or fabric surfaces, e.g., knit, woven, and non-woven surfaces (such as surgical garments, draperies, bed linens, bandages,

etc.), or patient-care equipment (such as respirators, diagnostic equipment, shunts, body scopes, wheel chairs, beds, etc.), or surgical and diagnostic equipment. Health care surfaces include articles and surfaces employed in animal health care.

As used herein, the term "instrument" refers to the various medical or dental instruments or devices that can benefit from cleaning with a composition according to the present invention.

As used herein, the phrase "meat product" refers to all forms of animal flesh, including the carcass, muscle, fat, organs, skin, bones and body fluids and like components that form the animal. Animal flesh includes, but is not limited to, the flesh of mammals, birds, fishes, reptiles, amphibians, snails, clams, crustaceans, other edible species such as lobster, crab, etc., or other forms of seafood. The forms of animal flesh include, for example, the whole or part of animal flesh, alone or in combination with other ingredients. Typical forms include, for example, processed meats such as cured meats, sectioned and formed products, minced products, finely chopped products, ground meat and products including ground meat, whole products, and the like.

As used herein, the phrases "medical instrument," "dental instrument," "medical device," "dental device," "medical equipment," or "dental equipment" refer to instruments, devices, tools, appliances, apparatus, and equipment used in medicine or dentistry. Such instruments, devices, and equipment can be cold sterilized, soaked or washed and then heat sterilized, or otherwise benefit from cleaning in a composition of the present invention. These various instruments, devices and equipment include, but are not limited to: diagnostic instruments, trays, pans, holders, racks, forceps, scissors, shears, saws (e.g. bone saws and their blades), hemostats, knives, chisels, rongeurs, files, nippers, drills, drill bits, rasps, burrs, spreaders, breakers, elevators, clamps, needle holders, carriers, clips, hooks, gouges, curettes, retractors, straightener, punches, extractors, scoops, keratomes, spatulas, expressors, trocars, dilators, cages, glassware, tubing, catheters, cannulas, plugs, stents, scopes (e.g., endoscopes, stethoscopes, and arthoscopes) and related equipment, and the like, or combinations thereof.

As used herein, the term "microorganism" refers to any noncellular or unicellular (including colonial) organism. Microorganisms include all prokaryotes. Microorganisms include bacteria (including cyanobacteria), spores, lichens, fungi, protozoa, virinos, viroids, viruses, phages, and some algae. As used herein, the term "microbe" is synonymous with microorganism.

As used herein, the terms "mixed" or "mixture" when used relating to "peroxycarboxylic acid composition" or "peroxycarboxylic acids" refer to a composition or mixture including more than one peroxycarboxylic acid, such as a composition or mixture including peroxyacetic acid (POAA) and peroxyoctanoic acid (POOA).

As used herein, the terms "mixed," "mixture" or "more than one" when used relating to esters suitable for use in forming the compositions of the invention refer to a composition or mixture including more than one ester group undergoing a perhydrolysis reaction to form the peroxycarboxylic composition. The use of at least one ester of a polyhydric alcohol and a C1 to C18 carboxylic acid according to the invention includes the use of various forms of the ester, such as the mono, di, tri and/or mixtures thereof formations of the particular ester. Accordingly, examples of suitable forms of esters for use as "mixtures" or comprising "more than one" include, but are not limited to, glycerol monooctanoate, glycerol dioctanoate, glycerol trioctanoate, sorbitan monooctanoate, sorbitan dioctanoate, sorbitan trioctanoate, and mixtures and derivatives thereof. Further, as one skilled in the art shall ascertain based upon the description of the invention disclosed herein, the use of an ester source, such as glycerol octanoate, may further comprise the use of the mono, di and tri esters and/or mixtures thereof. According to various embodiments of the invention, the use of "an" ester, such as octanoic glyceride, may include the use of a "mixture" of esters wherein more than one formation of the ester is present, including for example the mono, di and tri formations and/or mixtures thereof.

As used herein, the phrases "objectionable odor," "offensive odor," or "malodor," refer to a sharp, pungent, or acrid odor or atmospheric environment from which a typical person withdraws if they are able to. Hedonic tone provides a measure of the degree to which an odor is pleasant or unpleasant. An "objectionable odor," "offensive odor," or "malodor" has an hedonic tone rating it as unpleasant as or more unpleasant than a solution of 5 wt-% acetic acid, propionic acid, butyric acid, or mixtures thereof.

As used herein, the terms "peracid" or "peroxy acid" refer to an acid having the hydrogen of the hydroxyl group replaced by a hydroxy group. Oxidizing peracids are referred to herein as peroxycarboxylic acids.

As used herein, the phrase "plant" or "plant product" includes any plant substance or plant-derived substance. Plant products include, but are not limited to, seeds, nuts, nut meats, cut flowers, plants or crops grown or stored in a greenhouse, house plants, and the like. Plant products include many animal feeds.

As used herein, the term "polyhydric alcohol" or "polyol," refers to an alcohol that has two or more hydroxyl groups. Polyhydric alcohols suitable for use in the compositions include, but are not limited to, sugars, sugar alcohols, and mixtures and derivatives thereof.

As used herein the term "poultry" refers to all forms of any bird kept, harvested, or domesticated for meat or eggs, and including chicken, turkey, ostrich, game hen, squab, guinea fowl, pheasant, quail, duck, goose, emu, or the like and the eggs of these birds. Poultry includes whole, sectioned, processed, cooked or raw poultry, and encompasses all forms of poultry flesh, by-products, and side products. The flesh of poultry includes muscle, fat, organs, skin, bones and body fluids and like components that form the animal. Forms of animal flesh include, for example, the whole or part of animal flesh, alone or in combination with other ingredients. Typical forms include, for example, processed poultry meat, such as cured poultry meat, sectioned and formed products, minced products, finely chopped products and whole products.

As used herein, the phrase "poultry debris" refers to any debris, residue, material, dirt, offal, poultry part, poultry waste, poultry viscera, poultry organ, fragments or combinations of such materials, and the like removed from a poultry carcass or portion during processing and that enters a waste stream.

As used herein, the term "sanitizer" refers to an agent that reduces the number of bacterial contaminants to safe levels as judged by public health requirements. In an embodiment, sanitizers for use in this invention will provide at least a 99.999% reduction (5-log order reduction). These reductions can be evaluated using a procedure set out in *Germicidal and Detergent Sanitizing Action of Disinfectants*, Official Methods of Analysis of the Association of Official Analytical Chemists, paragraph 960.09 and applicable sections, 15th Edition, 1990 (EPA Guideline 91-2). According to this reference a sanitizer should provide a 99.999% reduction (5-log order reduction) within 30 seconds at room temperature, 25±2° C., against several test organisms.

As used in this invention, the term "sporicide" refers to a physical or chemical agent or process having the ability to cause greater than a 90% reduction (1-log order reduction) in the population of spores of *Bacillus cereus* or *Bacillus subtilis* within 10 seconds at 60° C. In certain embodiments, the sporicidal compositions of the invention provide greater than a 99% reduction (2-log order reduction), greater than a 99.99% reduction (4-log order reduction), or greater than a 99.999% reduction (5-log order reduction) in such population within 10 seconds at 60° C.

Differentiation of antimicrobial "-cidal" or "-static" activity, the definitions which describe the degree of efficacy, and the official laboratory protocols for measuring this efficacy are considerations for understanding the relevance of antimicrobial agents and compositions. Antimicrobial compositions can affect two kinds of microbial cell damage. The first is a lethal, irreversible action resulting in complete microbial cell destruction or incapacitation. The second type of cell damage is reversible, such that if the organism is rendered free of the agent, it can again multiply. The former is termed microbiocidal and the later, microbistatic. A sanitizer and a disinfectant are, by definition, agents which provide antimicrobial or microbiocidal activity. In contrast, a preservative is generally described as an inhibitor or microbistatic composition.

As used herein the term "sugar" refers to carbohydrates including one, two, or more saccharose groups. Sugars are a group of organic compounds related by molecular structure that comprise simpler members of the general class of carbohydrates. Each sugar consists of a chain of 2 to 7 carbon atoms (usually 5 or 6). Sugars have the general formula $C_2H_{2n}O_n$, wherein n is between 2 and 7. One of the carbons carries aldehydic or ketonic oxygen which may be combined in acetal or ketal forms and the remaining carbon atoms usually bear hydrogen atoms and hydroxyl groups. In general, sugars are more or less sweet, water soluble, colorless, odorless, optically active substances which lose water, caramelize and char when heated. Exemplary sugars include, but are not limited to, glucose, sucrose, lactose and mixtures thereof.

As used herein, the term "sugar alcohol" refers to the hydrogenated form of a carbohydrate, wherein the carbonyl group of the carbohydrate has been reduced to a primary or secondary hydroxyl group. Sugar alcohols have the general formula $CH_2OH(CHOH)_nCH_2OH$, wherein n is from 2 to 5. Exemplary sugar alcohols include, but are not limited to, glycol, ethylene glycol, propylene glycol, glycerol, erythritol, pentaerythritol, threitol, arabitol, xylitol, ribitol, mannitol, sorbitol, sorbitan, dulcitol, iditol, inositol, isomalt, maltitol, lactitol, polyglycitol, 1,4-cyclohexane diol, and mixtures and derivatives thereof. In some embodiments, the sugar alcohol is selected from ethylene glycol, propylene glycol, glycerol, polyglycerol, sorbitol, sorbitan, and mixtures and derivatives thereof.

As used herein, the term "ware" refers to items such as eating and cooking utensils, dishes, and other hard surfaces such as showers, sinks, toilets, bathtubs, countertops, windows, mirrors, transportation vehicles, and floors. As used herein, the term "ware washing" refers to washing, cleaning, or rinsing ware. Ware also refers to items made of plastic. Types of plastics that can be cleaned with the compositions according to the invention include but are not limited to, those that include polycarbonate polymers (PC), acrilonitrile-butadiene-styrene polymers (ABS), and polysulfone polymers (PS). Another exemplary plastic that can be cleaned using the compounds and compositions of the invention include polyethylene terephthalate (PET).

As used herein, the term "waters" includes food process or transport waters. Food process or transport waters include produce transport waters (e.g., as found in flumes, pipe transports, cutters, slicers, blanchers, retort systems, washers, and the like), belt sprays for food transport lines, boot and hand-wash dip-pans, third-sink rinse waters, and the like. Waters also include domestic and recreational waters such as pools, spas, recreational flumes and water slides, fountains, and the like.

As used herein, "weight percent," "wt-%," "percent by weight," "% by weight," and variations thereof refer to the concentration of a substance as the weight of that substance divided by the total weight of the composition and multiplied by 100. It is understood that, as used here, "percent," "%," and the like are intended to be synonymous with "weight percent," "wt-%," etc.

It should be noted that, as used in this specification and the appended claims, the singular forms "a," "an," and "the" include plural referents unless the content clearly dictates otherwise. Thus, for example, reference to a composition containing "a compound" includes a composition having two or more compounds. It should also be noted that the term "or" is generally employed in its sense including "and/or" unless the content clearly dictates otherwise.

EMBODIMENTS OF THE INVENTION

In some aspects, the present disclosure relates to a non-equilibrium or stoichiometric peroxycarboxylic acid forming compositions, and methods of making and using the compositions. Peroxycarboxylic acids are known for use as antimicrobials and bleaching agents. Conventional peroxycarboxylic acid compositions are formed through an acid catalyzed equilibrium reaction. Although acid catalyzed equilibrium reactions are commonly used to generate peroxycarboxylic acids, there are many downsides to such compositions, including, but not limited to the use of excess amounts of reactants required to drive the equilibrium reaction, along with the hazardous shipping conditions required to provide a customer the peroxycarboxylic acid compositions. The present compositions, and methods of forming them, according to the invention avoid these issues.

While an understanding of the mechanism is not necessary to practice the present invention and while the present invention is not limited to any particular mechanism of action, it is contemplated that, in some embodiments the benefits afforded according to the invention result from the production of a non-equilibrium chemistry. Beneficially, the reacted peracids according to the invention are obtained in greater amounts than in equilibrium chemistry wherein greater amounts of unreacted hydrogen peroxide and other reagents would be present. According to the present invention, an aqueous solution of the peroxycarboxylic acid(s) produced contains a relatively higher concentration of peroxycarboxylic acid(s) compared to unreacted hydrogen peroxide component. This is significantly advantageous for the antimicrobial, disinfectant, bleaching and other cleaning applications disclosed herein as desirable according to the embodiments of the invention.

In some aspects, the methods of the invention generate peracid from about 0.25% to about 20%. In some aspects, the methods of the invention generate peracid of about 2%, at least about 3%, preferably at least about 4%, more preferably at least about 5%, and still most preferably at least about 6% peracid from the reaction mixtures (reagents) according to the invention, namely the reaction of an ester or a mixture of esters of a polyhydric alcohol and a C1 to C18 carboxylic acid, a source of alkalinity, an oxidizing agent, and optionally an acidulating agent. Rather than providing a peracid com-

position in an equilibrium mixture, in situ generation of the peracid composition allows the peracids to be produced stoichiometrically through selecting the composition of the starting materials. The in situ systems according to the invention therefore generate higher concentrations of the peroxycarboxylic acid(s) than are available in equilibrium systems. In particular, according to the invention the systems generate higher concentrations of the peroxycarboxylic acid(s) and lower concentrations of hydrogen peroxide (e.g. unreacted reagents) than achieved in equilibrium systems. In addition, the methods of the present invention generate peroxycarboxylic acid(s) under alkaline conditions and thereafter adjust to acidic conditions to stabilize the peroxycarboxylic acid(s) and ensure the peroxycarboxylic acid(s) compositions do not disassociate, thereby providing stability for a sufficient amount of time to allow the use of the compositions on site after generation, preferably within a matter of hours or days.

As referred to herein, peroxycarboxylic acid forming compositions according to the invention refer to the generation of peroxycarboxylic acids in situ, in a non-equilibrium reaction. In particular embodiments of the invention, the methods produce the anion capable of forming peroxycarboxylic acid upon acidification. According to additional aspects of the invention, the methods may produce peroxycarboxylic acid compositions upon acidification.

Compositions

In some aspects, the present disclosure relates to peroxycarboxylic acid forming compositions. That is, the compositions are capable of generating peroxycarboxylic acids in situ, in a non-equilibrium reaction. Surprisingly, it has been found that the optimum pH for the generation of peroxycarboxylic acid compositions is greater than about 12, or pH greater than about 13. It has also been found that mixed peroxycarboxylic acid compositions, viz. compositions that form two or more peroxycarboxylic acids, can be generated in situ in accordance with the methods disclosed herein. Peroxycarboxylic (or percarboxylic) acids generally have the formula $R(CO_3H)n$, where, for example, R is an alkyl, aryl alkyl, cycloalkyl, aromatic, or heterocyclic group, and n is one, two, or three, and named by prefixing the parent acid with peroxy. The R group can be saturated or unsaturated as well as substituted or unsubstituted.

In an embodiment of the invention the peroxycarboxylic acid forming compositions comprise individual reagents combined according to the invention. These reagents are described herein individually along and include at least one ester of a polyhydric alcohol and a C1 to C18 carboxylic acid, an oxidizing agent, a source of alkalinity, solvents, and other functional groups. An acidulant is also described herein as a reagent to be added to the compositions after the formation of the percarboxylic acid(s). Alternatively, as described herein, there may be benefits to providing the reagents in various premix formulations to decrease the number of reagents and/or increase the simplicity of the invention. Each of these embodiments are described in further detail herein.

Esters

In some aspects, the compositions include an ester of a polyhydric alcohol and a C1 to C18 carboxylic acid. According to an embodiment, the polyhydric alcohol may also include a sugar alcohol. The compositions can also include more than one or a mixture of esters of a polyhydric alcohol and a C1 to C18 carboxylic acid. For example, in some embodiments, the compositions include two, three or four esters. When more than one ester is present, the esters can be different. For example, in some embodiments, the compositions can include a first ester of a polyhydric alcohol and a C1 to C4 carboxylic acid, and a second ester of a polyhydric alcohol and a C5 to C11 carboxylic acid. For further example, in some embodiments, the compositions can include a first ester of a polyhydric alcohol and a C1 to C18 carboxylic acid in a mono, di or tri-formation, and a second ester of a polyhydric alcohol and a C1 to C18 carboxylic acid in a mono, di or tri-formation. One skilled in the art will appreciate the various combinations of esters that can be used for the compositions according to the invention.

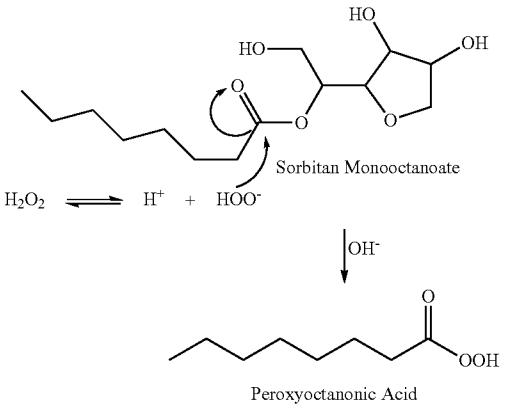
An example of a suitable ester for use according to the invention is glycerol octanoate. Glycerol octanoate has multiple ester components and others, including glycerol monooctanoate, glycerol dioctanoate, glycerol trioctanoate and others (glycerin, fatty acid, water). An estimated component percentage of each is approximated at about 39.6% glycerol monooctanoate, 24.5% glycerol dioctanoate, 1.42% glycerol trioctanoate and 34.5% of the others (glycerin, fatty acid, water).

The use of various forms of an ester (e.g. mono, di and/or tri-formations) to comprise a mixture of esters will impact the peracid yield of a particular composition according to the invention. For example, the various forms of the ester will have different kinetics in generating the peracids according to the methods of the invention. For example, in one aspect, a monooctanoate glycerol ester is faster in generating peracid than the di- or trioctanoate glycerol esters. In addition, the selection of the various forms of an ester will be further impacted by the water solubility of the compositions and whether any additional ingredients are combined to affect solubility (e.g. solvents) that would favor the use of less soluble ester forms (e.g. tri-formations). Accordingly, one skilled in the art of reaction kinetics will ascertain the benefits of using various combinations or mixtures of esters according to the compositions and methods of the invention.

The esters for use in the present invention include esters of polyhydric alcohols with carboxylic acid based leaving groups. A variety of carboxylic acids can be included. Carboxylic acids generally have the formula R(COOH)n, where, for example, R is an alkyl, aryl alkyl, cycloalkyl, aromatic, or heterocyclic group, and n is one, two, or three. In some embodiments, the carboxylic acid leaving group is a C_5 to C_{11} carboxylic acid. In some embodiments, the carboxylic acid leaving group is a C_1 to C_4 carboxylic acid. In other embodiments, the compositions include two esters of polyhydric alcohols, each ester having a different carboxylic acid leaving group. For example, the compositions can include a polyhydric alcohol ester with a C1 to C4 carboxylic acid leaving group, and also include a polyhydric alcohol ester with a C5 to C11 carboxylic acid leaving group.

Examples of suitable carboxylic acids include, but are not limited to, formic, acetic, propionic, butanoic, pentanoic, hexanoic, heptanoic, octanoic, nonanoic, decanoic, undecanoic, dodecanoic, as well as their branched isomers, lactic, maleic, ascorbic, citric, hydroxyacetic, neopentanoic, neoheptanoic, neodecanoic, oxalic, malonic, succinic, glutaric, adipic, pimelic subric acid, and mixtures thereof.

Without wishing to be bound by any particular theory, it is thought that the esters included in the compositions undergo a perhydrolysis reaction, thereby forming the peroxycarboxylic composition. An exemplary perhydrolysis reaction in accordance with the present disclosure is illustrated below:



As can be seen from this illustration, it is thought the oxidizing agent, H_2O_2, perhydrolyzes the ester bond, thereby forming the percarboxylic acid corresponding to the cleaved carboxylic acid group. In contrast to an acid catalyzed equilibrium reaction, the reaction is stoichiometric, i.e. no excess amounts of the reactants are required for the reaction. The kinetics of the reaction are pH dependent, and the reaction can reach the maximum yield in the order of minutes. Esters suitable for use include, but are not limited to, monooctanoic glyceride, dioctanoic glyceride, trioctaonoic glyceride, polyglycerol octanoate, sorbitan monooctanoate, sorbitan dioctanoate, sorbitan trioctanoate, laurate sucroside and mixtures and derivatives thereof.

The compositions include the esters in an amount sufficient to generate the desired amount of percarboxylic acid. In some embodiments, the compositions include about 0.01 wt-% to about 95 wt-% of the ester, about 0.1 wt-% to about 50 wt-% of the ester, or about 1 wt-% to about 10 wt-% of the ester. In some embodiments, more than one ester is present in the compositions. Each ester can be present in the compositions at the above stated weight percents.

Unlike conventional acid catalyzed equilibrium peroxycarboxylic acid forming compositions, the compositions of the present invention can be formed using a non-equilibrium perhydrolysis reaction. Thus, an excess amount of the starting reagents is not needed. Accordingly, after formation of the peroxycarboxylic acid, the compositions contain less carboxylic acid and more peroxycarboxylic acid than an equivalent equilibrium reaction. In some embodiments, the compositions contain about 1 part percarboxylic acid for every about 1 part carboxylic acid after perhydrolysis, or about 6 part percarboxylic acid for every about 1 part carboxylic acid after perhydrolysis. In some embodiments, the compositions are free of or substantially free of carboxylic acids after the perhydrolysis reaction.

Alkalinity Source

The compositions also include a source of alkalinity. The source of alkalinity can include, but is not limited to, an alkaline metal hydroxide, an alkaline earth metal hydroxide, an alkali metal silicate, an alkali metal carbonate, borates and mixtures thereof. Suitable alkaline metal hydroxides include, but are not limited to, sodium hydroxide, potassium hydroxide and mixtures thereof. Suitable alkaline earth metal hydroxides include, but are not limited to, magnesium hydroxide, calcium hydroxide and mixtures and derivatives thereof. Suitable alkali metal silicates include but are not limited to, sodium silicate and derivatives thereof. In other embodiments, an alkali metal carbonate can be used as a source of alkalinity. For example, in some embodiments, sodium carbonate, sodium bicarbonate or mixtures and derivatives thereof can be used.

The source of alkalinity can be present in the compositions in an amount sufficient to provide the desired pH. In some embodiments, the compositions have a pH greater than about 12, greater than about 12.5, or greater than about 13. In some embodiments, the alkaline source is present in the composition from about 0.001 wt-% to about 50 wt-%, from about 1 wt-% to about 30 wt-%, or about 10 wt-% to about 25 wt-%. In some embodiments, the alkaline source is present at from about 25 wt-% to about 50 wt-% of the composition. It is to be understood that all ranges and values between these ranges and values are encompassed by the present disclosure.

Oxidizing Agent

The compositions also include an oxidizing agent. The oxidizing agent may include a peroxide source. Oxidizing agents suitable for use with the compositions include the following types of compounds or sources of these compounds, or alkali metal salts including these types of compounds, or forming an adduct therewith: hydrogen peroxide, urea-hydrogen peroxide complexes or hydrogen peroxide donors of: group 1 (IA) oxidizing agents, for example lithium peroxide, sodium peroxide; group 2 (IIA) oxidizing agents, for example magnesium peroxide, calcium peroxide, strontium peroxide, barium peroxide; group 12 (IIB) oxidizing agents, for example zinc peroxide; group 13 (IIIA) oxidizing agents, for example boron compounds, such as perborates, for example sodium perborate hexahydrate of the formula $Na_2[B_2(O_2)_2(OH)_4]6H_2O$ (also called sodium perborate tetrahydrate); sodium peroxyborate tetrahydrate of the formula $Na_2B_2(O_2)_2[(OH)_4].4H_2O$ (also called sodium perborate trihydrate); sodium peroxyborate of the formula $Na_2[B_2(O_2)_2(OH)_4]$ (also called sodium perborate monohydrate); group 14 (IVA) oxidizing agents, for example persilicates and peroxycarbonates, which are also called percarbonates, such as persilicates or peroxycarbonates of alkali metals; group 15 (VA) oxidizing agents, for example peroxynitrous acid and its salts; peroxyphosphoric acids and their salts, for example, perphosphates; group 16 (VIA) oxidizing agents, for example peroxysulfuric acids and their salts, such as peroxymonosulfuric and peroxydisulfuric acids, and their salts, such as persulfates, for example, sodium persulfate; and group VIIa oxidizing agents such as sodium periodate, potassium perchlorate. Other active inorganic oxygen compounds can include transition metal peroxides; and other such peroxygen compounds, and mixtures thereof.

In some embodiments, the compositions of the present invention employ one or more of the inorganic oxidizing agents listed above. Suitable inorganic oxidizing agents include ozone, hydrogen peroxide, hydrogen peroxide adduct, group IIIA oxidizing agent, or hydrogen peroxide donors of group VIA oxidizing agent, group VA oxidizing agent, group VIIA oxidizing agent, or mixtures thereof. Suitable examples of such inorganic oxidizing agents include percarbonate, perborate, persulfate, perphosphate, persilicate, or mixtures thereof.

In some embodiments, the oxidizing agent includes hydrogen peroxide, or a source or donor of hydrogen peroxide. In other embodiments, the oxidizing agent includes a peroxide source selected from a percarbonate, a perborate urea hydrogen peroxide, PVP-peroxides and mixtures thereof.

The compositions may contain an effective amount of an oxidizing agent. In some embodiments, the compositions include about 0.001 wt-% to about 60 wt-% of the oxidizing agent, or about 1 wt-% to about 25 wt-% of the oxidizing agent. In some embodiments, the compositions include about 30 wt-% to about 50 wt-% of the oxidizing agent. It is to be

understood that all ranges and values between these ranges and values are encompassed by the present invention.

Solvent

In some embodiments, the compositions of the invention further include a solvent. In some embodiments, the solvent is water. The water may be provided by the use of aqueous reagents, viz. oxidizing agent, alkalinity source. In other embodiments, an additional amount of water is added to the compositions. The compositions may be free of or substantially free of any added water. A non-aqueous solvent may also be used in the compositions. For example, in some embodiments, an alcohol is included as a solvent in the compositions.

The compositions may include an effective amount of solvent. In some embodiments, the compositions may include about 10 wt-% to about 99 wt-% of a solvent, or about 20 wt % to about 80 wt-% of a solvent. In other embodiments, the compositions may include more than about 30 wt-%, more than about 50 wt-%, more than about 60 wt-% or more than 70% of a solvent. It is to be understood that all values and ranges between these values and ranges are encompassed by the present invention.

Eliminated Functional Ingredients

Unlike conventional equilibrium based peroxycarboxylic acid compositions, the compositions disclosed herein are formed from a non-equilibrium reaction. Further, the composition disclosed herein can be used immediately after generation. Thus, many of the additional ingredients required in equilibrium based compositions do not need to be included in the present compositions. In some embodiments stabilizing agents are preferred for certain compositions according to the invention and provide benefits. However, beneficially, the use of non-equilibrium chemistry according to the present invention optionally provides that the compositions can be free of, or substantially free of a stabilizing agent.

Stabilizing agents are commonly added to equilibrium peroxycarboxylic acid compositions to stabilize the peracid and hydrogen peroxide and prevent the decomposition of these constituents within the compositions. Various embodiments of the invention do not require the use of at least one or more of such stabilizing agents. Examples of stabilizing agents may include for example, surfactants, couplers, hydrotropes, acid catalysts and the like that are conventionally used in equilibrium peracid compositions to stabilize and improve shelf life of the composition.

Further examples of stabilizing agents include, for example, chelating agents or sequestrants. Such sequestrants include, but are not limited to, organic chelating compounds that sequester metal ions in solution, particularly transition metal ions. Such sequestrants include organic amino- or hydroxy-polyphosphonic acid complexing agents (either in acid or soluble salt forms), carboxylic acids (e.g., polymeric polycarboxylate), hydroxycarboxylic acids, aminocarboxylic acids, or heterocyclic carboxylic acids, e.g., pyridine-2,6-dicarboxylic acid (dipicolinic acid). Dipicolinic acid, 1-hydroxy ethylidene-1,1-diphosphonic acid (CH3C(PO3H2) 2OH) (HEDP) are further example of stabilizing agents.

Additional examples of stabilizing agents commonly used in equilibrium chemistry to stabilize the peracid and hydrogen peroxide and/or prevent the premature oxidation of the composition include phosphonic acid or phosphonate salt. Phosphonic acids and phosphonate salts include HEDP; ethylenediamine tetrakis methylenephosphonic acid (EDTMP); diethylenetriamine pentakis methylenephosphonic acid (DTPMP); cyclohexane-1,2-tetramethylene phosphonic acid; amino[tri(methylene phosphonic acid)]; (ethylene diamine[tetra methylene-phosphonic acid)]; 2-phosphene butane-1,2,4-tricarboxylic acid; or salts thereof, such as the alkali metal salts, ammonium salts, or alkyloyl amine salts, such as mono, di, or tetra-ethanolamine salts; picolinic, dipicolinic acid or mixtures thereof. In some embodiments, organic phosphonates, e.g., HEDP are well known as used stabilizing agents.

Exemplary commercially available food additive chelating agents include phosphonates sold under the trade name DEQUEST® including, for example, 1-hydroxyethylidene-1,1-diphosphonic acid, available from Monsanto Industrial Chemicals Co., St. Louis, Mo., as DEQUEST® 2010; amino (tri(methylenephosphonic acid)), ($N[CH_2PO_3H_2]_3$), available from Monsanto as DEQUEST® 2000; ethylenediamine [tetra(methylenephosphonic acid)] available from Monsanto as DEQUEST® 2041; and 2-phosphonobutane-1,2,4-tricarboxylic acid available from Mobay Chemical Corporation, Inorganic Chemicals Division, Pittsburgh, Pa., as Bayhibit AM. Further exemplary sequestrant can be or include aminocarboxylic acid type sequestrant. Suitable aminocarboxylic acid type sequestrants include the acids or alkali metal salts thereof, e.g., amino acetates and salts thereof. Suitable aminocarboxylates include N-hydroxyethylaminodiacetic acid; hydroxyethylenediaminetetraacetic acid, nitrilotriacetic acid (NTA); ethylenediaminetetraacetic acid (EDTA); N-hydroxyethyl-ethylenediaminetriacetic acid (HEDTA); diethylenetriaminepentaacetic acid (DTPA); and alanine-N, N-diacetic acid; and the like; and mixtures thereof. Still further sequestrants include polycarboxylates, including, for example, polyacrylic acid, maleic/olefin copolymer, acrylic/maleic copolymer, polymethacrylic acid, acrylic acid-methacrylic acid copolymers, hydrolyzed polyacrylamide, hydrolyzed polymethacrylamide, hydrolyzed polyamide-methacrylamide copolymers, hydrolyzed polyacrylonitrile, hydrolyzed polymethacrylonitrile, hydrolyzed acrylonitrile-methacrylonitrile copolymers, polymaleic acid, polyfumaric acid, copolymers of acrylic and itaconic acid, phosphino polycarboxylate, acid or salt forms thereof, mixtures thereof, and the like.

Further, unlike conventional equilibrium based peroxycarboxylic acid compositions, the present compositions can also be free of, or substantially free of surfactants. This is especially advantageous for compositions incorporating C5 to C18 peroxycarboxylic acids. That is, under perhydrolysis conditions, the C5-C18 peroxycarboxylic acid anions generated are water soluble. If the anions (e.g. peroxycarboxylic acid-forming compositions) are acidified for end use applications, the concentrations of peroxycarboxylic acids are below the water solubility limit of the peroxycarboxylic acids. Thus, couplers are not needed to couple the peroxycarboxylic acids in solution.

Additional Functional Ingredients

The compositions may also include additional functional ingredients. Additional functional ingredients suitable for use in the present compositions include, but are not limited to, acidulants, hydrotropes, dispersants, antimicrobial agents, optical tracers, solidification agent, aesthetic enhancing agent (i.e., colorant (e.g., pigment), odorant, or perfume), among any number of constituents which can be added to the composition. For example, suitable functional ingredients for various embodiments of the invention are hydrotropes, which may be desired for producing clear compositions or dispersants which are more efficient in producing homogeneous dispersions. Such adjuvants can be preformulated with the present compositions or added to the compositions after formation, but prior to use. The compositions can also contain

any number of other constituents as necessitated by the application, which are known and which can facilitate the activity of the present compositions.

Acidulant

In an embodiment, the present compositions can include an acidulant. The acidulant can be added to the compositions after the formation of the percarboxylic acid. That is, an acidulant can be added to the peroxycarboxylic acid concentrate to form an acidified use solution. The acidulant can be effective to form a use composition with pH of about 1 or less. The acidulant can be effective to form a use composition with pH of about 8, about 8 or less, about 7, about 7 or less, about 6, about 6 or less, about 5, about 5 or less, or the like. In some embodiments, the acidulant is present at an amount effective to form a use solution with a pH of about 6 to about 8, about 1 to about 8, or about 1 to about 5. In a further embodiment, the acidulant may be added to a semi-diluted reaction solution to produce meta-stable peracid composition.

Any suitable acid can be included in the compositions as an acidulant. In an embodiment the acidulant is an acid or an aqueous acidic solution. In an embodiment, the acidulant includes an inorganic acid. In some embodiments, the acidulant is a strong mineral acid. Suitable inorganic acids include, but are not limited to, sulfuric acid, sodium bisulfate, phosphoric acid, nitric acid, hydrochloric acid. In some embodiments, the acidulant includes an organic acid. Suitable organic acids include, but are not limited to, methane sulfonic acid, ethane sulfonic acid, propane sulfonic acid, butane sulfonic acid, xylene sulfonic acid, cumene sulfonic acid, benzene sulfonic acid, formic acid, acetic acid, mono, di, or tri-halocarboyxlic acids, picolinic acid, dipicolinic acid, and mixtures thereof. In some embodiments, the compositions of the present invention are free or substantially free of a phosphorous based acid.

In an embodiment, the acidulant includes a carboxylic acid with pK_a less than 5. Suitable carboxylic acids with pK_a less than 5 include acetic acid, hydroxyacetic acid, hydroxypropionic acid, other hydroxycarboxylic acids, mixtures thereof, or the like. Such an acidulant is present at a concentration where it does not act as a solubilizer. In some embodiments, the compositions are free of, or substantially free of a carboxylic acid.

In certain embodiments, the present composition includes about 0.001 to about 50 wt-% acidulant, about 0.001 to about 30 wt-% acidulant, about 1 to about 50 wt-% acidulant, about 1 to about 30 wt-% acidulant, about 2 to about 40 wt-% acidulant, about 2 to about 10 wt-% acidulant, about 3 to about 40 wt-% acidulant, about 5 to about 40 wt-% acidulant, about 5 to about 25 wt-% acidulant, about 10 to about 40 wt-% acidulant, about 10 to about 30 wt-% acidulant, about 15 to about 35 wt-% acidulant, about 15 to about 30 wt-% acidulant, or about 40 to about 60 wt-% acidulant. The composition can include any of these ranges or amounts not modified by about.

Premix Formulations

In an embodiment, the reagents described herein (e.g. at least one ester of a polyhydric alcohol and a carboxylic acid, source of alkalinity, oxidizing agent) may be combined into various premix formulations to reduce the number of raw starting materials required for the methods and compositions and further simplify the methods of the invention. According to such an embodiment the providing of premix formulations ensures consistent and stable delivery of reagents.

Premix formulations suitable for use according to the invention may comprise, consist of and/or consist essentially of at least one ester, an oxidizing agent and mixtures thereof. Premix formulations suitable for use according to the invention may comprise, consist of and/or consist essentially of at least one ester, an oxidizing agent, a solvent and mixtures thereof. Premix formulations suitable for use according to the invention may also comprise, consist of and/or consist essentially of at least one ester, an oxidizing agent, water, solvents, dispersing agents, and mixtures thereof.

As one skilled in the art will ascertain the use of premixes employs additional function ingredients for purpose of stabilizing the premix concentrate for use in the compositions and methods according to the invention. For example, hydrotropes, dispersing agents and/or other solvents may be desirable for maintaining the solubility and stability of a particular concentrated premix. The use of any couplers or dispersing agent (such as a surfactant) within a premix formulation is distinct from the use of surfactants in the conventional generation and storage of peracid chemistries, wherein couplers are critical to establishing and maintaining a stable, clear solution of the generated peracid chemistry.

According to the invention, the use of dispersing agents alone within a concentrated premix formulation does not stabilize the premix composition. Rather the dispersing agents are provided in an amount suitable for providing meta-stable peracid compositions generated from the premix after acidification, before further dilution for application. The most efficient dispersing agents were found to be anionic surfactants, and this type of surfactant is known to have high foaming profile. For applications which involves mechanical actions (e.g. CIP sanitizing), the high foam property of the composition is undesirable. Thus, in addition to economic reason, it is preferred to use a minimum amount of the dispersing agent to achieve a meta-stable peracid composition to meet the application of use requirements.

According to an embodiment of the invention less than about 10 ppm, preferably less than about 9 ppm, less than about 8 ppm, less than about 7 ppm, less than about 6 ppm, less than about 5 ppm, less than about 4 ppm, less than about 3 ppm, less than about 2 ppm, or less than about 1 ppm of a dispersing agent is included in the generated peracid chemistry as a result of the use of a surfactant dispersing agent in a concentrated premix formulation according to the invention. This is distinct from the level of surfactants in use solutions of a traditional peracid chemistry, where the amounts of surfactants are normally in excess of about 50 ppm, in excess of about 60 ppm, in excess of about 70 ppm, in excess of about 80 ppm, in excess of about 90 ppm, or in excess of about 100 ppm.

According to a further embodiment of the invention less than about 2% dispersing agent is present in the premix composition, wherein at least about 5%, about 6%, about 7%, about 8% or about 9% are required to provide the stable, clear solution of a generated peracid chemistry when acidified. This is distinct from the generated peracid chemistry according to the invention wherein a meta stable chemistry is generated. Although not wishing to be limited to a particular theory of mechanism of action of the invention, the generated meta-stable composition is a milky colored composition having stability for at least a few hours.

According to an embodiment of the invention, the use of a solvent (e.g. ethanol) is an efficient way to make a stable premix composition. Solvents suitable for the concentrated premix formulations according to the invention include, for example, organic solvents such as alcohol, ether or ketone. Preferably, the solvent is a water soluble alcohol, such as ethanol, methanol, propanol, isopropanol and/or butanol. As one skilled in the art will ascertain the various isomers of the solvents, including alcohols, are further included within the

scope of the solvents suitable for use with the concentrated premix formulations of the invention.

Beneficially, the use of concentrated premix formulation still does not require the use of any chelators and/or stabilizers. As a result, regardless of whether individual reagents or concentrated premix formulations are utilized according to the invention, both the reagents and the peracid compositions generated according to the invention provide sustainable chemistries as a result of the elimination of the use of various stabilizers and/or additional amounts of chemistry required to drive the formation of traditional peracid chemistry. As a result of reduced input of reagents for the compositions according to the invention (e.g. resulting from the use of a non-equilibrium reaction) there is a significantly reduced waste stream (e.g. any reagents and/or percentage of composition not impacting the micro-efficacy of the compositions). Instead the present invention provides increased amounts of post-reaction products (e.g. peracids) with decreased amounts of unreacted reagents.

In an aspect of the invention, a premix formulation may deliver the ester of a polyhydric alcohol and a carboxylic acid and the oxidizing agent. In one aspect a premix formulation includes an ester of a polyhydric alcohol and a carboxylic acid, an oxidizing agent and a dispersing agent. In another aspect a premix formulation includes an ester of a polyhydric alcohol and a carboxylic acid, an oxidizing agent, a dispersing agent and water.

Suitable dispersing agents for use according to the concentrated premix formulations of the invention include polymers, surface active agents or any compounds which will help to achieve a meta-stable solution after the ester perhydrolysis through the interaction with the peroxy fatty acids generated through perhydrolysis. These may include, for example, sulfonated oleic acids (SOA), 1-octanesulfonic acid (NAS), sodium lauryl sulfonates (SLS) and the like. In another aspect a premix formulation includes an ester of a polyhydric alcohol and a carboxylic acid, an oxidizing agent and a solvent. Ethanol and methanol are examples of suitable solvents for use in stabilizing the concentrated premix formulation according to the invention. The use of the solvent in certain embodiments obviates the use of a dispersing agent for premix stability. However, in alternative embodiments a premix formulation may include an ester of a polyhydric alcohol and a carboxylic acid, an oxidizing agent, a dispersing agent and a solvent. Without wishing to be limited to a particular theory or mechanism of action of the invention, the combined use of a dispersing agent and a solvent within a concentrated premix formulation reduces the overall need for a surfactant dispersing agent in the premix composition.

In still another aspect a concentrated premix formulation includes an oxidizing agent and a dispersing agent.

In certain embodiments, the concentrated premix composition includes about 0.001 to about 90 wt-% ester of the polyhydric alcohol and a carboxylic acid, about 0.1 to about 90 wt-% ester, about 1 to about 75 wt-% ester, about 10 to about 75 wt-% ester, about 25 to about 75 wt-% ester, about 30 to about 70 wt-% ester, or about 30 to about 65 wt-% ester.

In certain embodiments, the concentrated premix composition further includes about 0.001 to about 99 wt-% oxidizing agent, about 0.1 to about 95 wt-% oxidizing agent, about 1 to about 90 wt-% oxidizing agent, about 2.5 to about 60 wt-% oxidizing agent, about 5 to about 50 wt-% oxidizing agent, or about 10 to about 40 wt-% oxidizing agent.

In certain embodiments, the concentrated premix composition further includes about 0.001 to about 50 wt-% dispersing agent, about 0.1 to about 40 wt-% dispersing agent, about 1 to about 30 wt-% dispersing agent, about 5 to about 30 wt-% dispersing agent, about 5 to about 20 wt-% dispersing agent, or about 5 to about 15 wt-% dispersing agent. The amount of dispersing agent is selected to ensure that only enough dispersing agent to obtain a meta-stable solution after perhydrolysis and acidification. Beneficially according to the invention, the premix formulations do not contain sufficient dispersing agent to obtain a one phase premix solution.

In certain embodiments, the concentrated premix composition further includes about 0.001 to about 80 wt-% solvent, about 0.1 to about 40 wt-% solvent, about 1 to about 30 wt-% solvent, about 5 to about 30 wt-% solvent, about 5 to about 20 wt-% solvent, or about 5 to about 15 wt-% solvent. The level of solvent is selected to ensure the sufficient amount to solubilize the ester(s) of polyhydric alcohol in the concentrated premix formulation. As one skilled in the art will ascertain the amount of solvent required for such solubilization will vary depending upon the type and level of ester(s) in the premix composition.

In certain embodiments, the concentrated premix composition further includes about 0.001 to about 90 wt-% water, about 0.1 to about 80 wt-% water, about 1 to about 75 wt-% water, about 5 to about 60 wt-% water, about 10 to about 50 wt-% water, or about 20 to about 40 wt-% water. The premix compositions can include any of these ranges or amounts, including those not modified by about.

The pH of the concentrated premix formulation according to the invention is preferably between 2 and about 10, preferably between about 3 and about 9, and more preferably between about 5 and about 7. Thereafter the pH of the premix formulation is combined with an a source of alkalinity to increase the pH to a pH greater than about 12, greater than about 12.5, or greater than about 13 according to the invention.

Methods for Making, Using Individual Reagents

In some aspects, the present disclosure provides methods for making the peroxycarboxylic acid compositions disclosed herein. The method includes combining at least one ester of a polyhydric alcohol and a C1 to C18 carboxylic acid, a source of alkalinity and an oxidizing agent. This reaction mixture allows for the perhydrolysis of the ester to form the corresponding C1 to C18 peroxycarboxylic acid. Without wishing to be bound by any particular theory it is thought that the anion of the oxidizing agent (e.g. perhydroxide anion) present perhydrolyzes the ester bonds, thereby forming the corresponding percarboxylic acids.

In some embodiments, the pH of the reaction mixture is greater than about 12. In other embodiments, the reaction mixture is greater than about 12.5, or greater than about 13. The reagents can be combined in any suitable manner. Exemplary systems and methods for making the compositions are described in further detail in U.S. patent application Ser. Nos. 61/427,951 and 13/330,915, entitled Sugar Ester Peracid On-Site Generator and Formulator, U.S. patent application Ser. No. 13/330,981, entitled Continuous On-Line Adjustable Disinfectant/Sanitizer/Bleach Generator, and U.S. patent application Ser. No. 13/331,385, entitled Water Temperature as a Means of Controlling Kinetics of Onsite Generated Peracids, each filed concurrently herewith and incorporated by reference. For example, the reagents can be sequentially added to a reaction vessel, and mixed for an amount of time effective to form the desired percarboxylic acid concentration. Alternatively, the reagents can be added substantially simultaneously to a reaction vessel, and mixed for an amount of time effective to form the desired percarboxylic acid concentration. In some embodiments, the reagents are mixed for

about 5 to about 30 minutes. In other embodiments, the reagents are mixed for about 10, about 15, about 20, or about 25 minutes.

In some embodiments, a mixed percarboxylic acid composition is formed by using more than one ester of a polyhydric alcohol and a C1 to C18 carboxylic acid as starting reagents and/or more than form of an ester of a polyhydric alcohol and a C1 to C18 carboxylic acid as starting reagents (e.g. mono, di, tri or mixtures thereof for ester formations). For example, in some embodiments, a mixed percarboxylic acid composition including peracetic acid and peroctanoic acid is formed. To form this composition, an ester of a polyhydric alcohol and a C2 carboxylic acid is combined with an ester of a polyhydric alcohol and a C8 carboxylic acid, a source of alkalinity, and an oxidizing agent.

When forming a mixed peracid composition, the order of addition can be varied depending on the reaction conditions. For example, in some embodiments, all of the reagents can be combined and mixed in one step. Alternatively, in some embodiments, one of the esters can be added to a reaction vessel, with an oxidizing agent, and a source of alkalinity added sequentially. This mixture can be allowed to react for an effective amount of time, prior to the second ester being added to the reaction mixture. Preparing the mixed percarboxylic acid system in a stepwise manner also allows for control of the reaction temperature. For example, by splitting the perhydrolysis reactions into two steps, the overall temperature of the reaction mixture is lower.

The order of addition and time for reaction can be varied according to the desired percarboxylic acid composition. That is, the reaction can be controlled so as to favor the reaction conditions for formation of each of the percarboxylic acids individually. For example, if it is known that one of the esters has a kinetically slower perhydrolysis reaction rate, that ester can be added to the reaction vessel first. After an amount of time sufficient to maximize the percarboxylic acid formation of the first ester, the second ester with a kinetically faster perhydrolysis reaction rate can be added to the reaction vessel.

The order of mixing and addition of reagents can be used to control the production of the percarboxylic acid composition, namely to ensure a consistent output of chemistry without any fouling (e.g. precipitation) of the reagents. In one aspect of the invention, the source of alkalinity (e.g. sodium hydroxide or caustic soda) is combined with water (e.g. diluted) prior to the addition of the ester source.

The concentration of reagents, in addition to mixing order, can further be used to control the production of the percarboxylic acid composition. In a preferred embodiment, the concentration of the source of alkalinity is diluted to produce a consistent output of chemistry without any fouling (e.g. precipitation) of the reagents. In one aspect the concentrated alkaline solution (e.g. NaOH) is diluted with a water source before the ester component is combined with the reagents. Although not intending to be limited according to any theory of the invention and/or mechanism of action, the invention demonstrates superior chemistry generation when a system delivers a source of alkalinity (e.g. NaOH solution) that is no more than about 50%, preferably no more than about 40% on an actives basis before combining with the ester reagent to initiate the peracid production reaction.

In some aspects, the present disclosure provides methods for forming an antimicrobial and/or disinfecting composition. The methods include providing a mixed peroxycarboxylic acid forming composition. The mixed peroxycarboxylic acid forming composition includes: a first ester of a polyhydric alcohol and a C1 to C18 carboxylic acid, for example a C1 to C4 carboxylic acid; a second ester of a polyhydric alcohol and a C1 to C18 carboxylic acid, for example a C8 to C11 carboxylic acid; a source of alkalinity; and an oxidizing agent. After allowing the reaction mixture to react for a sufficient amount of time, a mixed percarboxylic acid composition is formed. The mixed peroxycarboxylic acid composition is diluted with an acidic aqueous solution. In some embodiments, the mixed peroxycarboxylic acid composition is diluted with an amount of an acidic aqueous solution effective to provide the diluted composition with a pH of about 1.0 to about 8.0. In other aspects, the present disclosure provides methods for forming a composition including a single percarboxylic acid. The methods include providing a peroxycarboxylic acid forming composition. The composition includes: an ester of a polyhydric alcohol and a C1 to C18 carboxylic acid; a source of alkalinity; and an oxidizing agent, wherein said composition has a pH greater than 12. The peroxycarboxylic acid forming composition is then diluted with an acidic aqueous solution. In some embodiments, the diluted acidic peroxycarboxylic acid composition has a pH of about 1.0 to about 8.0.

Any acidic solution can be used to dilute the peroxycarboxylic acid compositions. In an embodiment, the acidulant includes an inorganic acid. Suitable inorganic acids include, but are not limited to, sulfuric acid, sodium bisulfate, phosphoric acid, nitric acid, hydrochloric acid. In some embodiments, the acidulant includes an organic acid. Suitable organic acids include, but are not limited to, methane sulfonic acid, ethane sulfonic acid, propane sulfonic acid, butane sulfonic acid, xylene sulfonic acid, cumene sulfonic acid, benzene sulfonic acid, formic acid, acetic acid, mono, di, or tri-halocarboyxlic acids, picolinic acid, dipicolinic acid, and mixtures thereof. In some embodiments, the compositions of the present invention are free or substantially free of a phosphorous based acid.

In an aspect the acid or acidic solution acidifies the peroxycarboxylic acid forming composition to the peroxycarboxylic acid composition. In a further aspect, the use of an acid or acidic solution dilutes the peroxycarboxylic acid compositions. Methods employing the acidification of the peroxycarboxylic acid forming composition further stabilize the composition. However, as one skilled in the art will appreciate, some reaction intermediates of the peroxycarboxylic acid forming composition are stable for sufficient periods of time and do not need to be acidified immediately. For example, some reaction intermediates are stable for at least 24 hours and can be utilized in an on-site application without the acidification step for further dilution and/or stabilization. Other peroxycarboxylic acid forming compositions are less stable and the perhydrolysis reaction requires quenching with the acid or acidic aqueous solution to lower the pH and stabilize more promptly.

In another aspect of the invention, the peroxycarboxylic acid forming compositions are acidified within a cleaning application or within a use system (i.e., post generator within a customer's process). For example, post-generator acidification may include a clean in place (CIP) process where the peroxycarboxylic acid forming composition is pumped to a temporary holding tank for use in a CIP system, or pumped directly to a CIP system where the acid is added either in a pipe or the CIP vessel itself. A further example of post-generator acidification may include a healthcare application or certain laundry applications where the acid is added to provide a peroxycarboxylic acid (with an acid pH) to provide bleaching and/or sanitizing benefits of the peracid.

According to additional embodiments of the invention, there are various applications for the compositions of the

invention where acidification is not required and/or desired as the use of the peroxycarboxylic acid forming composition (anion solution) is preferred. For example, in a laundry application the acid is not be added in order to benefit from the alkaline pH of the anion for bleaching purposes. The alkaline pH for bleaching is obtained from the anion species, as a result the peroxycarboxylic acid forming composition does not have to be quenched with acid.

Methods for Making, Using Concentrated Premix Formulations

In additional aspects, the present disclosure provides methods for making the peroxycarboxylic acid compositions disclosed herein using concentrated premix formulations. Without limiting the scope of the invention and the methods for making the compositions disclosed herein, the same methods of making can be employed utilizing various concentrated premix formulations to combine the at least one ester of a polyhydric alcohol and a C1 to C18 carboxylic acid, a source of alkalinity and an oxidizing agent. The use of concentrated premix formulations minimizes the number of composition reagents according to the invention to simplify the methods even further.

The use of various concentrated premix formulations according to the invention does not alter the remaining method steps—only the input of the reagents into a system using the methods of the invention. Upon combining a particular concentrated premix formulation with the remaining reagents the reaction mixture allows for the perhydrolysis of the ester to form the corresponding C1 to C18 peroxycarboxylic acid. Without wishing to be bound by any particular theory it is thought that the oxidizing agent present (e.g. hydrogen peroxide or its anion) perhydrolyzes the ester bonds, thereby forming the corresponding percarboxylic acids.

According to an exemplary method of making the peroxycarboxylic acid compositions, a concentrated premix formulation comprising the ester(s) and oxidizing agent are mixed with the alkalinity source to form concentrated peracid chemistry. As disclosed herein, the alkalinity source may be an alkaline solution (e.g. NaOH) that is diluted with a water source before the concentrated premix comprising the ester component is combined with the dilute alkaline source.

The generated concentrated peracid chemistry according to the invention, regardless of whether generated using individual reagent sources and/or concentrated premix formulations, remains stable from a few hours to a few days. The on-site generated according to the invention obviates the need of various stabilizing agents as the chemistry is used on-site and not shipped and/or maintained in storage for any significant period of time.

The generated concentrated peracid chemistry may be diluted according to a particular use. For example, in an embodiment, the concentrated peracid chemistry is added to a post dilution tank or reservoir where water may be used to dilute the concentrated chemistry. This step may be referred to as generating an intermediate dilution. Without being limited to a particular theory of the invention, the dilution of the concentrated chemistry into an intermediate dilution in an alkaline solution maintains the phase stability of the peracid chemistry. In one aspect the solution may be diluted to about 100 ppm to about 10,000 ppm solution, preferably to about 1,000 ppm to about 4,000 ppm, and more preferably to about 1,000 ppm solution (e.g. about 0.1% active peracid). Thereafter the acidification of the diluted peracid chemistry may take place without any fouling of the chemistry. Thereafter the diluted peracid chemistry may be sourced to various use applications at very dilute amounts as a result of the on-site generation. For example, diluted peracid chemistry may be added into a use solution with concentrations less than about 10 ppm, less than about 50 ppm or less than about 100 ppm, without the wasteful shipment of such diluted chemistries.

As one skilled in the art will ascertain the method of making the peracid compositions, in particular the various dilutions of the concentrated peracid chemistries and/or acidification steps, may not be required depending upon the particular use applications of the chemistry. For example, a non-limiting example includes the use of a concentrated peracid chemistry for certain textile and/or bleaching applications. In such an embodiment, the concentrated peracid chemistry does not require the dilution in an alkaline solution to an intermediate solution having an active chemistry concentration of from about 100 ppm to about 10,000 ppm. Rather the concentrated alkaline chemistry could be immediately sourced to an application of use (e.g. textile cleaning and/or bleaching).

ILLUSTRATED EMBODIMENTS

FIG. **2** shows a diagram of an embodiment of certain methods of making the peracid chemistry according to the invention. As set forth therein, the methods of making the compositions include peracid generation which occurs through the dosing (e.g. injection) of raw starting materials (e.g. reagents) into a reaction vessel. The particular apparatuses and/or systems for the production of the chemistry are disclosed in the related applications set forth in the Cross Reference to Related Applications, which are incorporated herein by reference. In particular, the alkalinity source and water may be initially combined to obtain a diluted caustic source. According to a preferred embodiment, the caustic is diluted to a concentration of less than or equal to about 20% by weight. Thereafter, the ester and oxidizing source are combined with the diluted caustic for the perhydrolysis reaction to take place and generate the peracid composition. Thereafter, the reagents are held for the reaction to go to completion for a sufficient period of time. The next step involves the dilution of the concentrated peracid chemistry. In a further aspect the diluted chemistry can be acidified using an acid or aqueous acid solution.

Methods for Using

In some aspects, the present disclosure includes methods of using the peroxycarboxylic acid forming compositions disclosed herein. In some aspects, the methods of using the compositions employ a chemistry having a pH of from about 0 to about 5 for various antimicrobial and/or bleaching applications. In other aspects, the methods of using the compositions employ a chemistry having a pH of from about 5 to about 9 for various antimicrobial and/or bleaching applications. In still further aspects, the methods of using the compositions employ a chemistry having a pH of from about 5 to about 14 for various bleaching applications.

In some embodiments, these methods employ the antimicrobial and/or bleaching activity of the compositions. For example, the invention includes a method for reducing a microbial population, a method for reducing the population of a microorganism on skin, a method for treating a disease of skin, a method for reducing an odor, and/or a method for bleaching. These methods can operate on an article, surface, in a body or stream of water or a gas, or the like, by contacting the article, surface, body, or stream with the compositions. Contacting can include any of numerous methods for applying the compositions, such as spraying the compositions,

immersing the article in the compositions, foam or gel treating the article with the compositions, wiping the composition or a combination thereof.

In some aspects, the compositions are present at an amount effective for killing one or more of the food-borne pathogenic bacteria associated with a food product, including, but not limited to, *Salmonella typhimurium, Salmonella javiana, Campylobacter jejuni, Listeria monocytogenes*, and *Escherichia coli* O157:H7, yeast, and mold. In some embodiments, the compositions are present at an amount effective for killing one or more of the pathogenic bacteria associated with a health care surfaces and environments including, but not limited to, *Salmonella typhimurium, Staphylococcus aureus*, methicillin resistant *Staphylococcus aureus, Salmonella choleraesurus, Pseudomonas aeruginosa, Escherichia coli*, mycobacteria, yeast, and mold. The compositions of the present invention have activity against a wide variety of microorganisms such as Gram positive (for example, *Listeria monocytogenes* or *Staphylococcus aureus*) and Gram negative (for example, *Escherichia coli* or *Pseudomonas aeruginosa*) bacteria, yeast, molds, bacterial spores, viruses, etc. The compositions, as described above, have activity against a wide variety of human pathogens. The present compositions can kill a wide variety of microorganisms on a food processing surface, on the surface of a food product, in water used for washing or processing of food product, on a health care surface, or in a health care environment.

The compositions can be used for a variety of domestic or industrial applications, e.g., to reduce microbial or viral populations on a surface or object or in a body or stream of water. The compositions can be applied in a variety of areas including kitchens, bathrooms, factories, hospitals, dental offices and food plants, and can be applied to a variety of hard or soft surfaces having smooth, irregular or porous topography. Suitable hard surfaces include, for example, architectural surfaces (e.g., floors, walls, windows, sinks, tables, counters and signs); eating utensils; hard-surface medical or surgical instruments and devices; and hard-surface packaging. Such hard surfaces can be made from a variety of materials including, for example, ceramic, metal, glass, wood or hard plastic. Suitable soft surfaces include, for example paper; filter media; hospital and surgical linens and garments; soft-surface medical or surgical instruments and devices; and soft-surface packaging. Such soft surfaces can be made from a variety of materials including, for example, paper, fiber, woven or nonwoven fabric, soft plastics and elastomers. The compositions of the invention can also be applied to soft surfaces such as food and skin (e.g., a hand). The present compositions can be employed as a foaming or nonfoaming environmental sanitizer or disinfectant.

The compositions of the invention can be included in products such as sterilants, sanitizers, disinfectants, preservatives, deodorizers, antiseptics, fungicides, germicides, sporicides, virucides, detergents, bleaches, hard surface cleaners, hand soaps, waterless hand sanitizers, and pre- or post-surgical scrubs.

The compositions can also be used in veterinary products such as mammalian skin treatments or in products for sanitizing or disinfecting animal enclosures, pens, watering stations, and veterinary treatment areas such as inspection tables and operation rooms. The present compositions can be employed in an antimicrobial foot bath for livestock or people. The compositions can also be employed as an antimicrobial teat dip.

In some aspects, the compositions obtained according to the methods and apparatus of the present invention can be employed for reducing the population of pathogenic microorganisms, such as pathogens of humans, animals, and the like. The compositions exhibit activity against pathogens including fungi, molds, bacteria, spores, and viruses, for example, *S. aureus, E. coli, Streptococci, Legionella, Pseudomonas aeruginosa, mycobacteria, tuberculosis*, phages, or the like. Such pathogens can cause a variety of diseases and disorders, including mastitis or other mammalian milking diseases, tuberculosis, and the like. The compositions of the present invention can reduce the population of microorganisms on skin or other external or mucosal surfaces of an animal. In addition, the present compositions can kill pathogenic microorganisms that spread through transfer by water, air, or a surface substrate. The composition need only be applied to the skin, other external or mucosal surfaces of an animal water, air, or surface.

The compositions can also be used on foods and plant species to reduce surface microbial populations; used at manufacturing or processing sites handling such foods and plant species; or used to treat process waters around such sites. For example, the compositions can be used on food transport lines (e.g., as belt sprays); boot and hand-wash dip-pans; food storage facilities; anti-spoilage air circulation systems; refrigeration and cooler equipment; beverage chillers and warmers, blanchers, cutting boards, third sink areas, and meat chillers or scalding devices. The compositions can be used to treat produce transport waters such as those found in flumes, pipe transports, cutters, slicers, blanchers, retort systems, washers, and the like. Particular foodstuffs that can be treated with compositions of the invention include eggs, meats, seeds, leaves, fruits and vegetables. Particular plant surfaces include both harvested and growing leaves, roots, seeds, skins or shells, stems, stalks, tubers, corms, fruit, and the like. The compositions may also be used to treat animal carcasses to reduce both pathogenic and non-pathogenic microbial levels.

The compositions can also be used to treat waste water where both its antimicrobial function and its oxidant properties can be utilized. Aside from the microbial issues surrounding waste water, it is often rich in malodorous compounds of reduced sulfur, nitrogen or phosphorous. A strong oxidant such as the present invention converts these compounds efficiently to their odor free derivatives e.g. the sulfates, phosphates and amine oxides. These same properties are very useful in the pulp and paper industry where the property of bleaching is also of great utility.

In some aspects, the compositions of the present invention are useful in the cleaning or sanitizing of containers, processing facilities, or equipment in the food service or food processing industries. The compositions have particular value for use on food packaging materials and equipment, and especially for cold or hot aseptic packaging. Examples of process facilities in which the compositions can be employed include a milk line dairy, a continuous brewing system, food processing lines such as pumpable food systems and beverage lines, etc. Food service wares can be disinfected with the compositions. For example, the compositions can also be used on or in ware wash machines, low temperature ware wash machines, dishware, bottle washers, bottle chillers, warmers, third sink washers, cutting areas (e.g., water knives, slicers, cutters and saws) and egg washers. Particular treatable surfaces include packaging such as cartons, bottles, films and resins; dish ware such as glasses, plates, utensils, pots and pans; ware wash and low temperature ware wash machines; exposed food preparation area surfaces such as sinks, counters, tables, floors and walls; processing equipment such as tanks, vats, lines, pumps and hoses (e.g., dairy processing equipment for processing milk, cheese, ice cream and other dairy products); and trans-

portation vehicles. Containers include glass bottles, PVC or polyolefin film sacks, cans, polyester, PEN or PET bottles of various volumes (100 ml to 2 liter, etc.), one gallon milk containers, paper board juice or milk containers, etc.

The compositions can also be used on or in other industrial equipment and in other industrial process streams such as heaters, cooling towers, boilers, retort waters, rinse waters, aseptic packaging wash waters, and the like. The compositions can be used to treat microbes and odors in recreational waters such as in pools, spas, recreational flumes and water slides, fountains, and the like. The composition can also be used in treating microbes found in aqueous systems associated with petroleum or LP gas recovery or fermentation processes and pulp and paper processes and the like.

A filter containing peracid compositions of the present invention can reduce the population of microorganisms in air and liquids. Such a filter can remove water and air-borne pathogens such as *Legionella.*

The compositions obtained according to the methods and apparatus of the present invention can be employed for reducing the population of microbes, fruit flies, or other insect larva on a drain or other surface.

The compositions can also be employed by dipping food processing equipment into the use solution, soaking the equipment for a time sufficient to sanitize the equipment, and wiping or draining excess solution off the equipment, The compositions may be further employed by spraying or wiping food processing surfaces with the use solution, keeping the surfaces wet for a time sufficient to sanitize the surfaces, and removing excess solution by wiping, draining vertically, vacuuming, etc.

The compositions may also be used in a method of sanitizing hard surfaces such as institutional type equipment, utensils, dishes, health care equipment or tools, and other hard surfaces. The compositions of the present invention can also be used for laundry or textile applications. The compositions can be employed by rinsing laundry or textile surfaces with the use solution, keeping the surfaces wet for a sufficient time to wash, destain, sanitize, bleach and/or rinse the surface.

A concentrate or use concentration of the compositions can be applied to or brought into contact with an object by any conventional method or apparatus for applying an antimicrobial or cleaning compound to an object. For example, the object can be wiped with, sprayed with, foamed on, and/or immersed in the compositions, or a use solution made from the compositions. The compositions can be sprayed, foamed, or wiped onto a surface; the compositions can be caused to flow over the surface, or the surface can be dipped into the compositions. Contacting can be manual or by machine. Food processing surfaces, food products, food processing or transport waters, and the like can be treated with liquid, foam, gel, aerosol, gas, wax, solid, or powdered stabilized compositions according to the invention, or solutions containing these compounds.

Other hard surface cleaning applications for the compositions include clean-in-place systems (CIP), clean-out-of-place systems (COP), washer-decontaminators, sterilizers, textile laundry machines, ultra and nano-filtration systems and indoor air filters. COP systems can include readily accessible systems including wash tanks, soaking vessels, mop buckets, holding tanks, scrub sinks, vehicle parts washers, non-continuous batch washers and systems, and the like. CIP systems include the internal components of tanks, lines, pumps and other process equipment used for processing typically liquid product streams such as beverages, milk, juices.

A method of sanitizing substantially fixed in-place process facilities includes the following steps. A composition in accordance with various embodiments of the invention is introduced into the process facilities at a temperature in the range of about 4° C. to 60° C. After introduction of the composition, the solution is held in a container or circulated throughout the system for a time sufficient to sanitize the process facilities (e.g., to kill undesirable microorganisms). After the surfaces have been sanitized by means of the present compositions, the solution is drained. Upon completion of the sanitizing step, the system optionally may be rinsed with other materials such as potable water. The compositions can be circulated through the process facilities for 10 minutes or less.

The present methods can include delivering the present composition via air delivery to the clean-in-place or other surfaces such as those inside pipes and tanks. This method of air delivery can reduce the volume of solution required.

Methods for Contacting a Food Product

In some aspects, the present invention provides methods for contacting a food product with compositions according to the invention employing any method or apparatus suitable for applying such compositions. For example, in some embodiments, the food product is contacted by the compositions with a spray of the compositions, by immersion in the compositions, by foam or gel treating with the compositions. Contact with a spray, a foam, a gel, or by immersion can be accomplished by a variety of methods known to those of skill in the art for applying antimicrobial agents to food. Contacting the food product can occur in any location in which the food product might be found, such as field, processing site or plant, vehicle, warehouse, store, restaurant, or home. These same methods can also be adapted to apply the compositions of the present invention to other objects.

The present methods require a certain minimal contact time of the compositions with food product for occurrence of significant antimicrobial effect. The contact time can vary with concentration of the use compositions, method of applying the use compositions, temperature of the use compositions, amount of soil on the food product, number of microorganisms on the food product, type of antimicrobial agent, or the like. The exposure time can be at least about 5 to about 15 seconds. In some embodiments, the exposure time is about 15 to about 30 seconds. In other embodiments, the exposure time is at least about 30 seconds.

In some embodiments, the method for washing a food product employs a pressure spray including compositions of the present invention. During application of the spray solution on the food product, the surface of the food product can be moved with mechanical action, e.g., agitated, rubbed, brushed, etc. Agitation can be by physical scrubbing of the food product, through the action of the spray solution under pressure, through sonication, or by other methods. Agitation increases the efficacy of the spray solution in killing microorganisms, perhaps due to better exposure of the solution into the crevasses or small colonies containing the micro-organisms. The spray solution, before application, can also be heated to a temperature of about 15 to 20° C., for example, about 20 to 60° C. to increase efficacy. The spray stabilized compositions can be left on the food product for a sufficient amount of time to suitably reduce the population of microorganisms, and then rinsed, drained, or evaporated off the food product.

Application of the material by spray can be accomplished using a manual spray wand application, an automatic spray of food product moving along a production line using multiple spray heads to ensure complete contact, or other spray appa-

ratus. One automatic spray application involves the use of a spray booth. The spray booth substantially confines the sprayed compositions to within the booth. The production line moves the food product through the entryway into the spray booth in which the food product is sprayed on all its exterior surfaces with sprays within the booth. After a complete coverage of the material and drainage of the material from the food product within the booth, the food product can then exit the booth. The spray booth can include steam jets that can be used to apply the stabilized compounds of the invention. These steam jets can be used in combination with cooling water to ensure that the treatment reaching the food product surface is less than 65° C., e.g., less than 60° C. The temperature of the spray on the food product is important to ensure that the food product is not substantially altered (cooked) by the temperature of the spray. The spray pattern can be virtually any useful spray pattern.

Immersing a food product in the liquid compositions of the present invention can be accomplished by any of a variety of methods known to those of skill in the art. For example, the food product can be placed into a tank or bath containing the compositions. Alternatively, the food product can be transported or processed in a flume of the compositions. The washing solution can be agitated to increase the efficacy of the solution and the speed at which the solution reduces microorganisms accompanying the food product. Agitation can be obtained by conventional methods, including ultrasonics, aeration by bubbling air through the solution, by mechanical methods, such as strainers, paddles, brushes, pump driven liquid jets, or by combinations of these methods. The washing solution can be heated to increase the efficacy of the solution in killing micro-organisms. After the food product has been immersed for a time sufficient for the desired antimicrobial effect, the food product can be removed from the bath or flume and the compositions can be rinsed, drained, or evaporated off the food product.

In other embodiments, a food product can be treated with a foaming version of the compositions of the present invention. The foam can be prepared by mixing foaming surfactants with the washing solution at time of use. The foaming surfactants can be nonionic, anionic or cationic in nature. Examples of useful surfactant types include, but are not limited to the following: alcohol ethoxylates, alcohol ethoxylate carboxylate, amine oxides, alkyl sulfates, alkyl ether sulfate, sulfonates, including, for example, alkyl aryl sulfonates, quaternary ammonium compounds, alkyl sarcosines, betaines and alkyl amides. The foaming surfactant is typically mixed at time of use with the washing solution. Use solution levels of the foaming agents is from about 50 ppm to about 2.0 wt-%. At time of use, compressed air can be injected into the mixture, then applied to the food product surface through a foam application device such as a tank foamer or an aspirated wall mounted foamer.

In some embodiments, a food product can be treated with a thickened or gelled version of the compositions of the present invention. In the thickened or gelled state the washing solution remains in contact with the food product surface for longer periods of time, thus increasing the antimicrobial efficacy. The thickened or gelled solution will also adhere to vertical surfaces. The compositions can be thickened or gelled using existing technologies such as: xanthan gum, polymeric thickeners, cellulose thickeners, or the like. Rod micelle forming systems such as amine oxides and anionic counter ions could also be used. The thickeners or gel forming agents can be used either in the concentrated product or mixing with the washing solution, at time of use. Typical use levels of thickeners or gel agents range from about 100 ppm to about 10 wt-%.

Methods for Beverage, Food, and Pharmaceutical Processing

The compositions of the present invention can be used in the manufacture of beverage, food, and pharmaceutical materials including fruit juice, dairy products, malt beverages, soybean-based products, yogurts, baby foods, bottled water products, teas, cough medicines, drugs, and soft drinks. The compositions of the present invention can be used to sanitize, disinfect, act as a sporicide for, or sterilize bottles, pumps, lines, tanks and mixing equipment used in the manufacture of such beverages. Further, the compositions of the present invention can be used in aseptic, cold filling operations in which the interior of the food, beverage, or pharmaceutical container is sanitized or sterilized prior to filling. In such operations, a container can be contacted with the compositions, typically using a spray, dipping, or filling device to intimately contact the inside of the container with the compositions, for a sufficient period of time to reduce microorganism populations within the container. The container can then be emptied of the amount of sanitizer or sterilant used. After emptying, the container can be rinsed with potable water or sterilized water and again emptied. After rinsing, the container can be filled with the beverage, food, or pharmaceutical. The container can then be sealed, capped or closed and then packed for shipment for ultimate sale. The sealed container can be autoclaved or retorted for added microorganism kill.

In food, beverage, or pharmaceutical manufacturing, fungal microorganisms of the genus *Chaetomium* or *Arthrinium*, and spores or bacteria of the genus *Bacillus* spp. can be a significant problem in bottling processes, particularly in cold aseptic bottling processes. The compositions of the present invention can be used for the purpose of controlling or substantially reducing (by more than a 5 $\log_{10}$ reduction) the number of *Chaetomium* or *Arthrinium* or *Bacillus microorganisms* in beverage or food or pharmaceutical bottling lines using cold aseptic bottling techniques.

In such techniques, metallic, aluminum or steel cans can be filled, glass bottles or containers can be filled, or plastic (PET or PBT or PEN) bottles, and the like can be filled using cold aseptic filling techniques. In such processes, the compositions of the invention can be used to sanitize the interior of beverage containers prior to filling with the carbonated (or noncarbonated) beverage. Typical carbonated beverages in this application include, but are not limited to, cola beverages, fruit beverages, ginger ale beverages, root beer beverages, iced tea beverages which may be non-carbonated, and other common beverages considered soft drinks. The compositions of the invention can be used to sanitize both the tanks, lines, pumps, and other equipment used for the manufacture and storage of the soft drink material and also used in the bottling or containers for the beverages. In an embodiment, the compositions are useful for killing both bacterial and fungal microorganisms that can be present on the surfaces of the production equipment and beverage containers.

Methods for Industrial Processing

In some aspects, the invention includes methods of using the peroxycarboxylic acid forming compositions and/or peroxycarboxylic acids to prevent biological fouling in various industrial processes and industries, including oil and gas operations, to control microorganism growth, eliminate microbial contamination, limit or prevent biological fouling in liquid systems, process waters or on the surfaces of equipment that come in contact with such liquid systems. As

referred to herein, microbial contamination can occur in various industrial liquid systems including, but not limited to, air-borne contamination, water make-up, process leaks and improperly cleaned equipment. In another aspect, the peroxycarboxylic acid forming compositions and/or peroxycarboxylic acids are used to control the growth of microorganisms in water used in various oil and gas operations. In a further aspect, the compositions are suitable for incorporating into fracturing fluids to control or eliminate microorganisms.

For the various industrial processes disclosed herein, "liquid system" refers to flood waters or an environment within at least one artificial artifact, containing a substantial amount of liquid that is capable of undergoing biological fouling, it includes but is not limited to industrial liquid systems, industrial water systems, liquid process streams, industrial liquid process streams, industrial process water systems, process water applications, process waters, utility waters, water used in manufacturing, water used in industrial services, aqueous liquid streams, liquid streams containing two or more liquid phases, and any combination thereof.

In at least one embodiment this technology would be applicable to any process or utility liquid system where microorganisms are known to grow and are an issue, and biocides are added. Examples of some industrial process water systems where the method of this invention could be applied are in process water applications (flume water, shower water, washers, thermal processing waters, brewing, fermentation, CIP (clean in place), hard surface sanitization, etc.), Ethanol/Biofuels process waters, pretreatment and utility waters (membrane systems, ion-exchange beds), water used in the process/manufacture of paper, ceiling tiles, fiber board, microelectronics, E-coat or electro deposition applications, process cleaning, oil exploration and energy services (completion and work over fluids, drilling additive fluids, fracturing fluids, flood waters, etc.; oil fields—oil and gas wells/flow line, water systems, gas systems, etc.), and in particular water systems where the installed process equipment exhibits lowered compatibility to halogenated biocides.

Those skilled in the art will recognize, or be able to ascertain using no more than routine experimentation, numerous equivalents to the specific procedures, embodiments, claims, and examples described herein. Such equivalents are considered to be within the scope of this invention and covered by the claims appended hereto. The contents of all references, patents, and patent applications cited throughout this application are hereby incorporated by reference to the same extent as if each individual publication or patent application was specifically and individually indicated as incorporated by reference. All publications and patent applications in this specification are indicative of the level of ordinary skill in the art to which this invention pertains. The invention is further illustrated by the following examples, which should not be construed as further limiting.

EXAMPLES

Embodiments of the present invention are further defined in the following non-limiting Examples. It should be understood that these Examples, while indicating certain embodiments of the invention, are given by way of illustration only. From the above discussion and these Examples, one skilled in the art can ascertain the essential characteristics of this invention, and without departing from the spirit and scope thereof, can make various changes and modifications of the embodiments of the invention to adapt it to various usages and conditions. Thus, various modifications of the embodiments of the invention, in addition to those shown and described herein, will be apparent to those skilled in the art from the foregoing description. Such modifications are also intended to fall within the scope of the appended claims.

Example 1

A study was run to determine the ability to form peroxycarboxylic acids in situ from ester starting materials at alkaline pH levels. For this study, two different peroxycarboxylic acid forming compositions were each studied at two different pH levels. First, a peracetic acid (POAA) forming composition was tested at pH 12 and pH 13. For this test, 1.89 grams of hydrogen peroxide was mixed in a beaker with 0.62 grams of triacetin, 15 grams of distilled water, and 7.75 grams of a 10% solution of sodium hydroxide (NaOH). The beaker was fitted with a pH probe. After the sodium hydroxide was added the pH went up to about 12 immediately, and remained relatively stable while the sampling was performed. The peroxycarboxylic acid concentration was measured by removing a sample aliquot of the test solution, acidifying it with acetic acid, and titrating using an iodometric method. Both the peroxycarboxylic acid concentration and the hydrogen peroxide concentrations were measured over time. The above procedure was then repeated using an additional 11.71 grams of a 10% sodium hydroxide solution. This raised the pH to about 13 initially.

The above procedures were repeated twice using sorbitan caprylate instead of triacetin, to generate peroxyoctanoic acid (POOA) in situ. The peroxyoctanoic acid was also generated at both pH 12 and pH 13. The peroxycarboxylic acid concentration and hydrogen peroxide concentration of these test solutions was also measured over time. The results are shown in FIG. **1**.

As can be seen in FIG. **1**, the peroxyoctanoic acid generating solution was far more stable than the peracetic acid generating solution over time. This held true even for the elevated pH 13 test. Thus, as can be seen from this data, peroxyoctanoic acid can be generated in situ at relatively high pH levels, viz. pH about 13.

Example 2

A study was performed to evaluate the ability to generate a mixed peroxycarboxylic acid composition in situ from ester starting materials at alkaline pH. For this study, 1.28 grams of sorbitan octanoate, 14.68 grams of water, and 3.66 grams of a 35% hydrogen peroxide solution were added in a 100 mL beaker. With magnetic stirring, 14.64 grams of a 10% sodium hydroxide solution was added to the beaker. The solution was mixed for ten minutes. Then, 1.70 grams of triacetin was added to the solution. After mixing for an additional five minutes, the solution was sampled to measure the peroxyacetic (POAA) and peroxyoctanoic (POOA) acid concentrations.

This two-step addition process was also compared to a one step process. For the one step process, 1.26 grams of sorbitan octanoate, 1.70 grams of triacetin, 14.67 grams of water, and 3.66 grams of a 35% hydrogen peroxide solution were added in a 100 mL beaker. With magnetic stirring, 14.64 grams of a 10% sodium hydroxide solution was added to the beaker. After mixing for 15 minutes, the solution was sampled for POAA and POOA levels. The results for both the two step and the one step reaction methods are shown in the table below.

TABLE 1

Reaction Process	Peroxy-acetic Acid (wt-%)	Peroxy-octanoic Acid (wt-%)	Peroxyacetic/ Peroxyoctanoic (wt-% as Peroxy-acetic acid)	Temper-ature (maximum)	pH (initial-end)
Two Step	4.32	0.71	4.89	24.6° C.	12.19-11.47
One Step	3.95	0.60	4.33	28.1° C.	11.75-11.60

As can be seen from this table, the two step process delivered higher levels of POOA and POAA. It was also found that using the two step process described above generated lower temperatures than the one step process. These lower temperatures are important from both a safety and a stability standpoint for this reaction. Without wishing to be bound by any particular theory, it is thought that in the two step process, the kinetically slower perhydrolysis reaction of sorbitan octanoate was exposed to a more favorable perhydrolysis condition than in the one step reaction. That is in the two step process, the sorbitan octanoate is exposed to a higher pH and stoichiometrically more hydrogen peroxide. It is thought that these conditions contributed to the higher yield of POOA. Further, it is thought that the kinetically fast perhydrolysis reaction of triacetin was given enough perhydrolysis reaction time, but avoided a prolonged exposure to a high pH condition, and thus achieved a better POAA yield.

Example 3

A study was run to evaluate the ability to form a solid peroxycarboxylic acid forming composition. For this study, 2.5 grams of sorbitan octanoate was mixed with 2.5 grams of sodium bicarbonate in a beaker. Light sodium bicarbonate (2.5 grams) was then added. With stirring, the composition solidified quickly. Then, 2.5 grams of sodium percarbonate, and 1.04 grams of sodium hydroxide were added. The solid mixture was pressed in a mold with a 1.5 inch diameter, at a pressure of 2000 psi. A solid tablet was formed in one minute.

The solid was then added to 25 grams of deionized (DI) water, and stirred for 15 minutes. The solution was then sampled and measured for POOA concentration. The iodometric titration showed 1.08% POOA present in the solution. Thus, it was shown that a solid peroxycarboxylic acid forming composition can be generated in situ using an ester starting material.

Example 4

A study was run to evaluate the sanitizing efficacy of mixtures of peroxycarboxylic acids generated in situ from esters under alkaline conditions. For this study the following ester based peroxycarboxylic acid forming compositions were used.

TABLE 2

Peroxyoctanoic Premix (POOA)		Peroxyacetic Premix (POAA)	
Composition	Amount (g)	Composition	Amount (g)
Sorbitan octanoate	2.50	Triacetin	4.90
35% Hydrogen Peroxide	2.26	35% Hydrogen Peroxide	10.58
Water	15.16	Water	42.31
10% NaOH	10.74	10% NaOH	42.21

The above Peroxycarboxylic acid premixes were then tested alone at various concentrations, and mixed at various concentrations against *Staphylococcus aureus* ATCC 6538, and *Escherichia coli* ATCC 11229. The compositions tested are shown in the table below.

TABLE 3

Test Substance	Tested Concentration	Diluent	Test Solution (Volume of Test Substance/Total Volume)	pH
POOA	13 ppm	500 ppm	0.18 g/300 g	4.98
POAA	61 ppm	Synthetic Hard	0.64 g/300 g	5.00
POOA +	13 ppm +	Water (pH	0.32 g + 1.07	4.99
POAA	61 ppm	7.80)	g/500 g	
POAA	35 ppm		0.21 g/300 g	5.00
POOA	15 ppm		0.37 g/300 g	5.01
	20 ppm		0.45 g/300 g	4.98
POOA +	20 ppm +		0.45 g + 0.26	4.99
POAA	15 ppm		g/500 g	
	15 ppm +		0.35 g + 0.62	5.01
	35 ppm		g/500 g	

The test substances were tested against *Staphylococcus aureus* ATCC 6538, and *Escherichia coli* ATCC 11229 at 25° C.±1° C. for 30 seconds. A neutralizer screen was performed as part of the testing to verify that the neutralizer adequately neutralized the product and was not detrimental to the tested organisms. The inoculum numbers are shown in the table below.

TABLE 4

Test System	CFU/mL	Log_{10} Growth	Average Log_{10} growth
Staphylococcus aureus ATCC 6538,	9.3×10^7	7.97	7.97
	9.5×10^7	7.98	
Escherichia coli ATCC 11229	1.10×10^8	8.04	8.05
	1.17×10^8	8.07	

The results from the various test substances are shown in the tables below.

TABLE 5

Staphylococcus aureus ATCC 6538

Test Substance	Exposure Time	Survivors (CFU/mL)	Average Log_{10} Survivors	Log Reduction
13 ppm POOA + 61 ppm POAA	30 seconds	1.0×10^1, $<1.0 \times 10^1$	1.00	6.97
20 ppm POOA + 15 ppm POAA	30 seconds	$<1.0 \times 10^1$, $<1.0 \times 10^1$	<1.00	>6.97
15 ppm POOA + 35 ppm POAA	30 seconds	$<1.0 \times 10^1$, $<1.0 \times 10^1$	<1.00	>6.97

TABLE 6

Escherichia coli ATCC 11229

Test Substance	Exposure Time	Survivors (CFU/mL)	Average Log_{10} Survivors	Log Reduction
13 ppm POOA pH 4.98	30 seconds	4.22×10^7, 3.52×10^7	7.59	0.46
61 ppm POAA pH 5.00	30 seconds	3.0×10^3, 2.4×10^4	3.93	4.12
13 ppm POOA + 61 ppm POAA	30 seconds	$<1.0 \times 10^1$, $<1.0 \times 10^1$	<1.00	>7.05

TABLE 6-continued

Escherichia coli ATCC 11229

Test Substance	Exposure Time	Survivors (CFU/mL)	Average Log_{10} Survivors	Log Reduction
pH 4.99 35 ppm POAA	30 seconds	1.85×10^7, 1.86×10^7	7.27	0.78
pH 5.00 15 ppm POOA	30 seconds	1.06×10^7, 1.83×10^7	7.15	0.90
pH 5.01 20 ppm POOA	30 seconds	7.0×10^5, 7.0×10^5	5.85	2.20
pH 4.98 20 ppm POOA + 15 ppm POAA	30 seconds	$<1.0 \times 10^1$, $<1.0 \times 10^1$	<1.00	>7.05
15 ppm POOA + 35 ppm POAA	30 seconds	$<1.0 \times 10^1$, $<1.0 \times 10^1$	<1.00	>7.05

As can be seen from these results, at every concentration tested, POOA and POAA alone at pH 5.0 failed the sanitizer test with less than 5 log reductions of *Escherichia coli* after 30 seconds. A passing result for a sanitizing efficacy screen requires a greater than 5 log reduction in test system growth after a 30 second exposure time. However, a synergistic effect was observed between POOA and POAA when mixed together. For example a complete kill of both *Staphylococcus aureus* and *Escherichia coli* was observed after a 30 second exposure time with the mixed systems.

Example 5

A study was run to evaluate the ability to form peroxycarboxylic acids from ester starting materials in various solvents. First, a test was run to determine the ability to form a peroxycarboxylic acid (POOA) from glyceryl trioctanoate using water as the solvent. For this test, 2.50 grams of glyceryl trioctanoate was added to 2.25 grams of 35% hydrogen peroxide. Then, 30 grams of deionized water, and 10.50 grams of a 10% aqueous sodium hydroxide solution were added. All of these components were added in serial fashion to a 150 mL Pyrex beaker fitted with a magnetic stir bar. Just prior to the addition of the sodium hydroxide, stirring was initiated and maintained through all of the subsequent addition steps. Samples of the reaction solution were taken at 15, 27, and 40 minutes. The samples were treated with acetic acid, and titrated using an iodometric peroxycarboxylic acid titration to measure the peroxycarboxylic acid concentration. The results are shown in Table 7.

A comparative example was then run using a semi-methanolic reaction solution. For this comparative example, 2.50 grams of glyceryl trioctanoate was added to 2.25 grams of 35% hydrogen peroxide followed by 30 grams of 100% methanol, and 10.50 grams of a 10% aqueous sodium hydroxide solution. All of these components were added in serial fashion to a 150 mL Pyrex beaker fitted with a magnetic stir bar. Just prior to the addition of the sodium hydroxide, stirring was initiated and maintained through all of the subsequent steps. Samples of the reaction solution were taken at 10, 20, and 30 minutes and treated with acetic acid and titrated using a standard iodometric peroxycarboxylic acid titration. The results from this semi-methanolic reaction solution comparative example are also shown in Table 7.

Finally, another comparative example was run using a purely alcoholic reaction solution. For this comparative example, 2.50 grams of glyceryl trioctanoate was added to 6.75 grams of 10% urea-hydrogen peroxide-ethanol solution followed by 30 grams of 100% methanol, and 14.70 grams of a 10% potassium hydroxide/methanol solution. All of these components were added in serial fashion to a 150 mL Pyrex beaker fitted with a magnetic stir bar. Just prior to the addition of the potassium hydroxide solution, stirring was initiated and maintained through all of the subsequent steps. Samples of the reaction solution were taken at 8, 26, 47, and 69 minutes. The samples were treated with acetic acid, and titrated using a standard iodometric peroxycarboxylic acid titration to measure for peroxycarboxylic acid concentration. The results are also shown in Table 7 below.

TABLE 7

Reaction Time (min)	Purely Aqueous Reaction Solution POOA (%)	Purely Aqueous Reaction Solution Portion Converted (%)	Semi-Methanolic Reaction Solution POOA (%)	Semi-Methanolic Reaction Solution Portion Converted (%)	Pure Methanolic Reaction Solution POOA (%)	Pure Methanolic Reaction Solution Portion Converted (%)
8					1.59	34.0
10			1.00	18.0		
15	0.00	0.00				
20			1.89	34.0		
26					1.69	36.1
27	0.00	0.00				
30			2.32	42.0		
40	0.00	0.00				
47					1.59	34.0
69					1.59	34.0

As can be seen from this table, in a purely aqueous reaction, no POOA was formed. Without wishing to be bound by any particular theory, it is thought that the HLB of glyceryl trioctanoate is too low (less than 3). That is, the low water solubility/dispersability of glyceryl trioctanoate prohibits the perhydrolysis reaction in the purely aqueous environment, regardless of the otherwise favorable perhydrolysis conditions. This surprising result is true for sugar esters in general with an HLB less than 3. For example, sorbitan trioctanoate (HLB less than 3) could not be perhydrolized in an aqueous solution to generate peroxyoctanoic acid, however, sorbitan monooctanoate (HLB greater than 3) was readily perhydrolysibile in aqueous solutions.

Example 6

A single peracid chemistry (POOA) was generated according to the invention using the reagents set forth in Table 8A. POOA production rates were generated as a function of reagents and generator temperatures. A continuous ABF generator was used wherein both the reagent and reaction vessels temperature were controlled with a heating/cooling water bath as set forth in Table 8B. The results demonstrate the POOA production as a function of time.

TABLE 8A

Reagent Formula		Amt (%)
ABF POOA	Glycerol Octanoate	14.67%
	H_2O_2 35%	19.42%
	Water	49.44%
	NaOH 50%	16.47%

TABLE 8B

5° C. Rxn		20° C. Rxn		30° C. Rxn		40° C. Rxn	
time	% POOA 5° C.	time	% POOA 20° C.	Time	% POOA 30° C.	time	% POOA 40° C.
10	2.55	1	2.07	1		1	5.19
20	3.45	5	3.89	3	4.56	3	6.23
30	3.90	10	4.77	5	5.24	5	6.06
40	4.20	15	5.46	10	6.35	7	5.36
50	4.20	20	5.83	15	6.57	10	5.40
60	4.50	25	6.30	20	6.52	15	3.38
70	4.72	30	6.67	30	6.29	20	3.82
		40	6.77	45	5.60		
		50	6.73	90	4.36		
		70	6.61				
		90	6.36				
		160	5.66				

The results are shown in FIG. **3** (graphical representation of POOA concentration over time at various reaction temperatures). The graph confirms that under different environmental temperatures the concentration of available peracid is widely variable. The variability depends upon the temperature of the generator and temperature of the reactants (e.g. raw starting materials) and of the time point at which the reaction mixture would be used. These results demonstrate the importance of mechanisms for controlling the ex-situ peracid reaction temperature. The control of temperature impacts the kinetics of the reaction and therefore can be critical to consistency of peracid output according to the invention.

Example 7

Methods of thermal control were analyzed. The reaction rates of a single peracid chemistry (POOA) generated according to the invention were analyzed. The reagents set forth in Table 9A were used to generate POOA. The test utilized reactants that were stored at either 5° C. or 40° C. (as further shown in Table 9B) to represent the changes in (and ranges of) temperatures one skilled in the art may expect in practice.

TABLE 9A

Reagent Formula		Amt (%)
ABF POOA	Glycerol Octanoate	9.83%
	H_2O_2 35%	13.02%
	Water (21.1° C.)	65.90%
	NaOH 50%	11.21%

The test controlled the temperature of the reaction by controlling the vessel temperature where the reaction took place. The temperature was controlled to 20° C. (~69° F.). In this reaction the glycerol octanoate, peroxide and water reagents (e.g. raw starting materials) were added to the reaction vessel first. Once those ingredients were combined the 50% NaOH was added. For purposes of testing this reaction scheme was utilized as a result of the addition of NaOH both initiating the reaction and causing a large exothermic effect. Both temperature and resultant peracid were monitored in this reaction.

POOA production rates and temperature were monitored as a function of time with reaction vessel temperatures controlled to 20° C., wherein the reagents were stored at either 5° C. or 40° C. The results are shown in Table 9B.

TABLE 9B

time (min)	temp with 5° C. reagents	temp with 40° C. reagents	POOA @ 5° C.	POOA @ 40° C.
0	69	84	0	0
1	80	84	0.73	0.95
3	72	73	1.36	1.58
5	70	71	1.69	1.90
10	69	69	2.28	2.44
20	69	69	2.80	3.04
30	69	69	3.22	3.50
45	69	69	3.72	3.98
60	69	69	4.02	4.24
90	69	69	4.30	4.23
120	69	69	4.03	4.00
180	69	69		3.57

The results are further shown in the graph of FIG. **4**. The identified time period from approximately 50 minutes to 120 minutes (shown in the boxed area of the graph) outlines where the 2 separate reaction mixtures (one with reagents starting at 5° C. and one with reagents starting at 40° C.) achieved maximum percentage POOA generation. These results demonstrate the ability to use temperature control as a means of driving toward consistency in the chemistry output 9 without regard to environmental temperatures under which the chemistry production takes place.

This example required increased time to achieve maximum generation of the peracid chemistry, notably about 50 minutes to achieve the +/−10% max target for peracid generation. However, as one skilled in the art of chemical reaction kinetics will ascertain, to decrease the time period for achieving maximum peracid generation the temperature of the reaction vessel and/or reaction manifold can be increased.

Example 8

Additional methods of thermal control were analyzed. The thermal control scheme outlined in Example 7 may add cost and/or complexity to an ABF system. As a result, improvements to the various methods for including temperature control were analyzed. An alternative was evaluated—heating one or more of the raw starting materials (i.e. reagents) for the ex-situ peracid composition. The heating of reagents as opposed to the reaction vessel where the chemical reaction is housed was evaluated as a means to control the reaction kinetics.

In this analysis water was selected as the raw starting material that was temperature controlled. Water was selected based on the fact that water tends to be the most abundant reagent in many peracid recipes according to the invention. In addition, the heating of water can be easily and inexpensively achieved as one skilled in the art will appreciate.

The reagents set forth in Table 10A were used to generate POOA.

TABLE 10A

Reagent Formula		Amt (%)
ABF POOA	Glycerol Octanoate	9.83%
	H_2O_2 35%	13.02%
	Water	65.90%
	NaOH 50%	11.21%

Table 10B shows the POOA production rates and temperature as a function of time with reagent temperatures controlled to variable temperatures −5° C. and 40° C., as opposed

to temperature control of the reaction vessel and/or reaction manifold. The results are shown in Table 10B.

TABLE 10B

time (min)	POOA 5° C. reagents	POOA 40° C. reagents	Rxn Temp 5° C. reagents	Rxn Temp 40° C. reagents
0	0	0	89	94
1	1.26	1.65	109	117
3	2.30	2.68	106	112
5	2.82	3.16	103	108
10	3.56	3.65	96	100
15	3.70	3.87	85	94
20	3.83	3.83	87	89
30	3.92	3.76	80	81
45	3.90	3.63	74	75
60	3.80	3.52	72	72
90	3.62		72	

The results are further shown in the graph of FIG. **5**. The results demonstrate the potential to use a heated water source to produce reaction kinetic rates with no other temperature controls of a system for generating the chemistry according to the invention.

Example 9

Concentrated premix formulations according to the invention were evaluated for peracid generation. The following premixes were utilized to generate the perhydrolysis compositions and final peracid concentrations set forth in Table 11.

TABLE 11

Premix	Premix Components	Wt-%	Perhydrolysis Composition	Wt-%	Rxn Time (minutes)	Peracid %
SOA Premix	Glycerol Octanoate	47.48	SOA Premix	27.60	5	3.93
	H_2O_2 (50%)	39.58	NaOH (50%)	13.45		
	Sulfonated Oleic Acid (SOA) (70%)	12.95	Water	58.95		
NAS Premix	Glycerol Octanoate	32.78	NAS premix	36.84	5	4.22
	H2O2 (50%)	30.36	NaOH (50%)	13.78		
	1-Octanesulfonic acid, sodium salt (40%)	14.52	Water	49.38		
	Water	22.34				
Ethanol Premix	Glycerol Octanoate	48.09	Ethanol Premix	27.60	5	5.20
	H_2O_2 (50%)	40.09	NaOH (50%)	13.45		
	Ethanol	11.82	Water	58.95		
SLS-Ethanol Premix	Glycerol Octanoate	46.40	SLS-Ethanol premix	24.85	8	4.03
	H_2O_2 (50%)	38.68	NaOH (50%)	12.12		
	SLS (30%)	7.10	Water	63.03		
	Ethanol	7.82				
SLS-Ethanol Premix 2	Glycerol Octanoate	47.17	SLS-Ethanol premix	27.31	8	5.41
	H_2O_2 (50%)	39.27	NaOH (50%)	13.32		
	SLS (30%)	5.42	Water	59.37		
	Ethanol	8.13				
SLS-H_2O_2 Premix	H_2O_2 (35%)	91.19	Glycerol Octanoate	12.88	8	5.17
	SLS (30%)	8.81	SLS-H2O2 premix	16.80		
			NaOH (50%)	13.32		
			Water	57.00		

The results of Table 11 show the various examples of concentrated premix formulations suitable for use according to the invention. The premix is provided in a concentrated formulation and then added to the remaining perhydrolysis composition as shown in the table. The premix formulation is diluted with the remaining reagents of the perhydrolysis composition, which is often referred to as a tank dilution. The perhydrolysis composition is then allowed to react for the time shown therein.

The resultant percentage of peracid generated in the chemistry is further shown demonstrating the utility of premix formulations for the generation of peracid chemistries according to the invention.

Example 10

The use of premix formulations for generating chemistry according to the invention was evaluated to determine the stability of various premix compositions as shown in Table 12. The use of a surfactant in premix formulation according to the invention includes a dispersant-effective amount for the meta-stability of the generated peracid solution (e.g. acidified), not the stability of the premix formulation. Accordingly, the use of a surfactant premix according to the invention, such as an ethanol-SLS premix (as outlined in Example 9) uses the surfactant (e.g. SLS) only for the physical stability of the perhydrolysis reaction mixture. In one tested embodiment, the amount of surfactant in the premix (less than about 2%) is significantly less than the levels needed to achieve a clear, transparent premix (at least about 9%). This result is from the ethanol solvent being the primary contributor of the premix stability. The surfactant-bleach activator interaction in the tested premix is in sufficient to generate a homogeneous premix.

Similarly, the use of a solvent premix, such as an ethanol premix, according to the invention does not include a dispersing agent.

TABLE 12

Premix	Premix Components	Wt %	Physical Appearance
Ethanol Premix	Glycerol Octanoate	48.09	Clear one phase
	H2O2 (50%)	40.09	
	Ethanol	11.82	

TABLE 12-continued

Premix	Premix Components	Wt %	Physical Appearance
SLS—Ethanol Premix	Glycerol Octanoate	47.17	Clear one phase
	H2O2 (50%)	39.27	
	Ethanol	8.13	
	SLS (30%)	5.42	
SLS—Premix	Glycerol Octanoate	47.17	Two phases
	H2O2 (50%)	39.27	
	Water	8.13	
	SLS (30%)	5.42	

Example 11

Perhydrolysis studies at varying pH ranges were evaluated. In particular, the perhydrolysis rates of the ester source Monocaprin-100 (Abitec), a glycerol monooctanoate as a function of pH were evaluated. The reagents set forth in Table 13A were used to generate POOA according to the pH and formulations reacted to different stop times set forth in Table 13B. Table 13C shows the percentage of peracid generated after acidification at varying reaction stop times at the different pH.

TABLE 13A

	Amt (%)
Monocaprin-100	10.1
H_2O_2 35%	13.37%
Water	18.94%
NaOH 10%	57.6%

TABLE 13B

pH	NaOH used, g	Makeup DI-H2O, g	start time, min	stop times, min 10 min	20 min	30 min
12.45	57.6	0.00	0	10	20	30
11.45	34.6	23.00	2	12	22	32
11.04	26.6	31.00	4	14	24	34

TABLE 13C

Sample	pH	Perhydrolysis Time: (% POOA post quench) (minutes of reaction) 10	20	30	MG pot MG %	MG pot POOA %	DG pot DG %	DG pot POOA %	Tot. Pot. POOA %	Yield of Pot. %
#1	12.45	2.20%	2.84%	2.89%	38.20%	2.83	15.60%	1.47	4.30	67%
#2	11.45	1.32%	1.45%	1.52%	38.20%	2.83	15.60%	1.47	4.30	35%
#3	11.04	0.88%	0.84%	0.71%	38.20%	2.83	15.60%	1.47	4.30	17%

The results are shown in FIG. **6** wherein the varying amounts of peracid (POOA) generated are compared to the reacted pH. The results indicate the benefit of undergoing the perhydrolysis reaction to generate peracid at a pH above 12, preferably above about 12.5. While it is not surprising that perhydrolysis processes are sped up at higher pHs, it is surprising that the degradation rate is significantly slower from pH 11.04 to pH 12.45.

Example 12

A variety of surfactants were analyzed for coupling and/or dispersion stabilizing of a peroxycarboxylic acid composition generated according to the methods of the invention. In particular, a peroxyoctanoic acid (POOA) composition in deionized water produced according to the invention was analyzed for coupling and/or dispersion stabilization using the dispersing agents set forth in Table 14A.

Given the very limited water solubility of POOA in its protonated form, acidification of the alkaline perhydrolysis solutions of the same causes immediate precipitation and rapid phase separation. In this example various surfactants and hydrotropes were evaluated for their ability to couple the POOA. In Table 14A it can be seen that the most efficient agents for coupling an already precipitated solution of POOA were samples I and II. SLS and LAS showed the greatest efficacy in coupling and dispersion of the POOA solutions, requiring 0.64 g/200 g aqueous POOA.

TABLE 14A

Sample	(A) Concentration of POOA (ppm) in DI Water	(B) Surfactant-Dispersant	Amount of (B) Required for Coupling (g/200 g aq POOA)
I	1000	Sodium Lauryl Sulfate (SLS)	0.64
II	1000	Linear Aryl Sulfonate (LAS)	0.65
III	1000	Sodium Lauryl Ether Sulfate (SLES)	>0.94
IV	1000	Pluronic 25R2 (AE)	>>0.74
V	1000	Amine oxide (AO)	>3.58
VI	1000	Alkyl Polyglycosides (APG)	2.46
VII	1000	Sodium octanesulfonate (NAS-FAL)	6.60
VIII	1000	Sorbitan monolaurate ethoxylate (Tween 20)	>2.59
IX	1000	Alcohol ethoxylate (Pluronic L24-5)	>2.0
X	1000	Sodium dioctyl Sulfosuccinates (NaDOSS)	>2.0

The SLS, LAS and SOA dispersing agents were then further examined for efficacy in stabilizing and/or dispersing in 1% or lower sulfuric acid solutions. Solutions were made according to the following order (3, 6, 9, 12, 1, 4, 7, 10, 2, 5, 8, 11, 13, 14). Solution 13 was made as 1 through 12 with the addition of 50 mL of 5 grain hard water to the aliquot of alkaline reaction solution followed by swirling with the surface aliquot and then additional 50 mL of 5 grain hard water, followed within about 5 seconds by 50 mL of 5 grain 2% sulfuric acid and swirled. Solution 14 was made by direct addition of 1% sulfuric acid (5 grain) without pre-dilution,

but after moments of swirling with SLS aliquot. All concentrations are shown in ppm.

For the POOA solutions the targeted peracid concentration was based upon initial average of about 5.40 wt-% of ongoing cold alkaline peracid hydrolysis according to the invention (**), wherein the aliquot was constant while POOA was increasing.

While coupling in this case is defined as clarifying or reducing the opacity of an otherwise cloudy POOA solution, the same surfactants were found to be very efficient at stabilizing acidic, aqueous dispersions of POOA as shown in Table 14B. The appearance of an oil sheen was regarded as a pass or fail. From this data it can be seen that SLS is an exceptional dispersant for acidified POOA.

TABLE 14B

	**POOA	H_2SO_4	LAS	SOA	SLS		oil sheen at 1 h	oil sheen at 23 h	Bulk POOA at 15 min	Bulk POOA at 1 h	Bulk POOA at 23 h	Rxn sol'n POOA
1	1,000	10,000	100			dense cloudy	no	yes				5.78% to 5.92%
2	1,000	10,000		100		dense cloudy	no	yes				5.92% to 6.11%
3	1,000	10,000			100	light cloudy	no	no	1054	981	638	5.40% to 5.78%
4	1,000	10,000	200			dense cloudy	no	yes				5.78% to 5.92%
5	1,000	10,000		200		dense cloudy	no	yes				5.92% to 6.11%
6	1,000	10,000			200	almost clear	no	no	1055	1016	523	5.40% to 5.78%
7 (control)	750	10,000	100			dense cloudy	no	* yes				5.78% to 5.92%
8	750	10,000		100		dense cloudy	no	yes				5.92% to 6.11%
9	750	10,000			100	light cloudy	no	no	773	748	408	5.40% to 5.78%
10	750	10,000	200			dense cloudy	no	yes				5.78% to 5.92%
11	750	10,000		200		dense cloudy	no	yes				5.92% to 6.11%
12	750	10,000			200	almost clear	no	no	802	734	323	5.40% to 5.78%
***13	1,000	10,000	none	none	none	Initially cloudy	yes	yes				5.40%
****14	750	10,000			100	semi dense cloudy	no	no				

Table 14B shows that the only non-SLS dispersing agent that approaches the passing of stability of the POOA solution at 23 hours is LAS, demonstrating minimal surface oil (*). The inventions being thus described, it will be obvious that the same may be varied in many ways. Such variations are not to be regarded as a departure from the spirit and scope of the inventions and all such modifications are intended to be included within the scope of the following claims.

What is claimed is:

1. A peroxycarboxylic acid forming composition comprising:

a first reagent premix comprising at least one ester of a polyhydric alcohol and a C5 to C18 carboxylic acid with HLB value of 3 or greater, an organic solvent selected from the group consisting of methanol, ethanol, propanol, isopropanol, butanol, an ether, a ketone, and combinations thereof, wherein said organic solvent solubilizes the ester; a dispersing agent, wherein the dispersing agent is a sulfonated oleic acid, 1-octanesulfonic acid, or sodium lauryl sulfonates; and one or more agents selected from the group consisting of an oxidizing agent, water, and mixtures thereof; wherein the dispersing agent is sufficient to create a physically meta-stable solution upon reaction with a source of alkalinity; and

a second reagent source comprising the source of alkalinity; wherein said composition is not at equilibrium, and has a pH greater than 12.

2. The composition of claim **1**, wherein the carboxylic acid comprises a C5 to C18 carboxylic acid and wherein the polyhydric alcohol is selected from the group consisting of a sugar, a sugar alcohol, and mixtures and derivatives thereof.

3. The composition of claim **1**, wherein the polyhydric alcohol is selected from the group consisting of ethylene glycol, propylene glycol, glycerol, sorbitol, sorbitan, and mixtures and derivatives thereof and wherein the ester is

selected from the group consisting of glycerol monooctanoate, glycerol dioctanoate, glycerol trioctanoate, sorbitan monooctanoate, sorbitan dioctanoate, sorbitan trioctanoate, laurate sucroside and mixtures and derivatives thereof and wherein the oxidizing agent comprises a hydrogen peroxide donor.

4. The composition of claim **1**, wherein the oxidizing agent comprises hydrogen peroxide or a source of hydrogen peroxide selected from the group consisting of a percarbonate, a perborate, urea hydrogen peroxide, PVP-peroxides and mixtures thereof.

5. The composition of claim **1**, wherein the source of alkalinity is selected from the group consisting of an alkaline metal hydroxide, an alkaline earth metal hydroxide, an alkali metal silicate, an alkali metal carbonate, borates and mixtures thereof.

6. The composition of claim **1**, wherein the reagent premix consists of at least one ester of a polyhydric alcohol and a C5 to C18 carboxylic acid with HLB value of 3 or greater, an oxidizing agent, a dispersing agent, and a solvent.

7. The composition of claim **6**, wherein the reagent premix consists of at least one ester of a polyhydric alcohol and a C5 to C18 carboxylic acid with HLB value of 3 or greater, an oxidizing agent, and a dispersing agent.

8. A peroxycarboxylic acid forming composition comprising:

a first reagent premix comprising at least one ester of a polyhydric alcohol and a C5 to C18 carboxylic acid with HLB value of 3 or greater, an organic solvent selected from the group consisting of methanol, ethanol, propanol, isopropanol, butanol, an ether, a ketone, and combinations thereof, an oxidizing agent and a dispersing agent; wherein the dispersing agent is a sulfonated oleic acid, 1-octanesulfonic acid, or sodium lauryl sulfonates and in an amount sufficient to create a physically meta-stable solution upon reaction with a source of alkalinity; wherein said organic solvent solubilizes the ester; and

a second reagent source comprising a source of alkalinity; wherein said composition is not at equilibrium, and has a pH greater than 12.

9. The composition of claim **8**, wherein the first reagent premix comprises an ester of a C5 to C11 carboxylic acid, and further comprises a C1 to C4 carboxylic acid ester, wherein at least one ester has an HLB value of 3 or greater, and wherein the esters are selected from the group consisting of glycerol monooctanoate, glycerol dioctanoate, glycerol trioctanoate, sorbitan monooctanoate, sorbitan dioctanoate, sorbitan trioctanoate, laurate sucroside and mixtures and derivatives thereof.

10. The composition of claim **9**, wherein the reagent premix further comprises water.

11. The composition of claim **8**, wherein the oxidizing agent comprises hydrogen peroxide or a hydrogen peroxide source selected from the group consisting of a percarbonate, a perborate, urea hydrogen peroxide, PVP-peroxides and mixtures thereof.

12. The composition of claim **8**, wherein the source of alkalinity is selected from the group consisting of an alkaline metal hydroxide, an alkaline earth metal hydroxide, an alkali metal silicate, an alkali metal carbonate and mixtures thereof.

13. The composition of claim **8**, wherein the reagent premix comprises glycerol octanoate and hydrogen peroxide.

14. The composition of claim **13**, wherein the reagent premix comprises glycerol octanoate, hydrogen peroxide, sodium lauryl sulfonate and an alcohol solvent.

15. A method for delivering an antimicrobial a surface comprising providing a single or mixed peroxycarboxylic acid antimicrobial composition formed by diluting a composition first reagent premix comprising at least one ester of a polyhydric alcohol and a C5 to C18 carboxylic acid with HLB value of 3 or greater, an organic solvent selected from the group consisting of methanol, ethanol, propanol, isopropanol, butanol, an ether, a ketone, and combinations thereof, an oxidizing agent, and a dispersing agent, and a second reagent source comprising a source of alkalinity, with an aqueous acidic solution to a pH of about 1 to about 8, wherein the solvent is an organic solvent to solubilize the ester; and wherein the dispersing agent is a sulfonated oleic acid, 1-octanesulfonic acid, or sodium lauryl sulfonates and in an amount sufficient to create a physically meta-stable solution upon reaction with a source of alkalinity.

16. A method for forming an antimicrobial composition, said method comprising:

(a) providing a peroxycarboxylic acid composition having active peroxycarboxylic acid content from about 0.25% to about 20% comprising:

(i) a first reagent premix comprising at least one ester of a polyhydric alcohol and a C5 to C18 carboxylic acid with HLB value of 3 or greater, an organic solvent selected from the group consisting of methanol, ethanol, propanol, isopropanol, butanol, an ether, a ketone, and combinations thereof, a dispersing agent, and one or more agents selected from the group consisting of an oxidizing agent, water, and mixtures thereof; wherein the solvent solubilizes the ester; wherein the dispersing agent is a sulfonated oleic acid, 1-octanesulfonic acid, or sodium lauryl sulfonates and in an amount sufficient to create a physically meta-stable solution upon reaction with a source of alkalinity; and

(ii) a second reagent source comprising a source of alkalinity; wherein said composition has a pH greater than 12 and is not at equilibrium;

(b) diluting the generated peroxycarboxylic acid composition to an active peroxycarboxylic acid content from about 0.01% to about 1%;

(c) providing an acidic aqueous solution; and

(d) diluting the peroxycarboxylic acid composition with the acidic aqueous solution to a pH of about 1.0 to about 8.0 to form the antimicrobial composition.

17. The method of claim **16**, wherein the peroxycarboxylic acid composition is allowed to react for a sufficient amount of time such that a C5 to C18 percarboxylic acid is formed.

18. The method of claim **17**, wherein the peroxycarboxylic acid composition has a pH greater than about 12.5 and wherein the dilution of the peroxycarboxylic acid composition generates an active peroxycarboxylic acid content of about 0.01% to about 0.1%.

19. The method of claim **18**, wherein the antimicrobial composition having a pH of about 1.0 to about 8.0 is further diluted to a use solution having an active peroxycarboxylic acid content of about 1 ppm to about 100 ppm.

20. A method for forming an antimicrobial composition, said method comprising:

(a) providing a peroxycarboxylic acid composition having active peroxycarboxylic acid content from about 0.25% to about 20% comprising:

(i) a first reagent premix comprising at least one ester of a polyhydric alcohol and a C5 to C18 carboxylic acid with HLB value of 3 or greater, an organic solvent selected from the group consisting of methanol, ethanol, propanol, isopropanol, butanol, an ether, a ketone, and combinations thereof, a dispersing agent, and one or more agents selected from the group con-

sisting of an oxidizing agent, water, and mixtures thereof; wherein the dispersing agent is a sulfonated oleic acid, 1-octanesulfonic acid, or sodium lauryl sulfonates and in an amount sufficient to create a physically meta-stable solution upon reaction with a source of alkalinity; and

(ii) a second reagent source comprising a source of alkalinity; wherein said composition has a pH greater than 12 and is not at equilibrium;

(b) allowing the peroxycarboxylic acid composition to react for a sufficient amount of time such that a C5 to C18 percarboxylic acid is formed to generate a antimicrobial composition; and

(c) providing antimicrobial composition to an application for use without an acidification step.

21. The method of claim **20**, wherein the antimicrobial composition is further diluted within a use application.

22. The method of claim **20**, wherein the antimicrobial composition is substantially free of a stabilizing agent.

* * * * *

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[54] **PEROXYACID ANTIMICROBIAL COMPOSITION**

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[57] **ABSTRACT**

A peroxyacid antimicrobial concentrate and use composition is provided comprising a C_1 to C_4 peroxycarboxylic acid, and a C_6 to C_{18} peroxyacid. The combination of these acids produces a synergistic effect, providing a much more potent biocide than can be obtained by using these components separately. Other components can be added to the composition such as hydrotrope coupling agents, stabilizers, etc. An effective antimicrobial use solution is formed at low concentrations when the concentrate composition is diluted with water to a pH in the range of about 2 to 8. Sanitizing of substantially fixed, "in-place" processing lines in dairies, breweries, and other food processing operations is one utility of the composition.

12 Claims, No Drawings

EXHIBIT
I

PEROXYACID ANTIMICROBIAL COMPOSITION

FIELD OF THE INVENTION

The invention relates generally to antimicrobial or biocidal compositions. More particularly, the invention relates to peroxyacid antimicrobial concentrates and use solutions which can sanitize various surfaces such as facilities and equipment found in the food processing and food service industries, and various inanimate surfaces in the health care industry.

BACKGROUND OF THE INVENTION

Numerous classes of chemical compounds exhibit varying degrees of antimicrobial or biocidal activity. Antimicrobial compositions are particularly needed in the food and beverage industries to clean and sanitize processing facilities such as pipelines, tanks, mixers, etc. and continuously operating homogenation or pasteurization apparatus. Sanitizing compositions have been formulated in the past to combat microbial growth in such facilities. For example, Wang, U.S. Pat. No. 4,404,040, teaches a short chain fatty acid sanitizing composition comprising an aliphatic short chain fatty acid, a hydrotrope solubilizer capable of solubilizing the fatty acid in both the concentrate and use solution, and a hydrotrope compatible acid so that the use solution has a pH in the range of 2.0 to 5.0.

Peroxy-containing compositions are known for use in the production of microbicidal agents. One such composition is disclosed in Bowing et al., U.S. Pat. No. 4,051,059 containing peracetic acid, acetic acid or mixtures of peracetic and acetic acid, hydrogen peroxide, anionic surface active compounds such as sulfonates and sulfates, and water.

Peracetic acid has been shown to be a good biocide, but only at fairly high concentrations (generally greater than 100 part per million (ppm)). Similarly, peroxyfatty acids have also been shown to be biocidal, but only at high concentrations (greater than 200 ppm), such as in the composition disclosed in European Patent Application No. 233,731.

Antimicrobial compositions having low use concentrations (less than 100 ppm) which effectively kill microbes are particularly desirable. Low concentrations minimize use cost, surface corrosion, odor, carryover of biocide into foods and potential toxic effects to the user. Therefore, a continuing need exists to provide such an antimicrobial composition for use in food processing, food service and health care facilities. In contrast to the prior art, the composition of the present invention has the unique advantage of having antimicrobial or biocidal activity at low level use concentrations.

SUMMARY OF THE INVENTION

The invention is a peroxyacid antimicrobial concentrate and diluted end use composition comprising an effective microbicidal amount of a C_1–C_4 peroxycarboxylic acid, and an effective microbicidal amount of a C_6–C_{18} peroxyacid. The concentrate composition can be diluted with a major proportion of water to form an antimicrobial sanitizing use solution having a pH in the range of about 2 to 8, with a C_1–C_4 peroxycarboxylic acid concentration of at least about 10 ppm, preferably about 10 to 75 ppm, and a C_6–C_{18} peroxyacid concentration of at least about 1 ppm, preferably about 1 to 25 ppm. Other components may be added such as a hydrotrope coupling agent for solubilizing the peroxyfatty acid in the concentrate form and when the concentrate composition is diluted with water.

In contrast to the prior art, we have discovered that at a low pH, (e.g. preferably less than 5) C_6–C_{18} peroxyacids such as peroxyfatty acids are very potent biocides at low levels. When used in combination with a C_1–C_4 peroxycarboxylic acid such as peroxyacetic acid, a synergistic effect is obtained, providing a much more potent biocide than can be obtained by using these components separately. This means that substantially lower concentrations of biocide can be used to obtain equal cidal effects, leading to lower costs of the product and less potential for corrosion.

As the term is used herein, a C_6–C_{18} peroxyacid (or peracid) is intended to mean the product of the oxidation of a C_6–C_{18} acid such as a fatty acid, or a mixture of acids, to form a peroxyacid having from about 6 to 18 carbon atoms per molecule. The C_1–C_4 peroxycarboxylic acid is intended to mean the product of oxidation of a C_1–C_4 carboxylic acid, or a mixture thereof. This includes both simple and substituted C_1–C_4 carboxylic acids.

A method of sanitizing facilities or equipment comprises the steps of contacting the facilities or equipment with the use solution made from the above concentrate composition of the invention at a temperature in the range of about 4° to 60° C. The composition is then circulated or left in contact with the facilities or equipment for a time sufficient to sanitize (generally at least 30 seconds) and the composition is thereafter drained or removed from the facilities or equipment.

One aspect of the invention is the novel, antimicrobial concentrate composition which is capable of being diluted with a major proportion of water to form a sanitizing use solution. A further aspect of the invention is an aqueous antimicrobial sanitizing use solution which is particularly suited for "in-place" cleaning applications. A further aspect of the invention is a method of employing the use solution of the invention in the cleaning or sanitizing of various process facilities or equipment as well as other surfaces.

DETAILED DESCRIPTION OF THE INVENTION

The invention resides in a peroxyacid antimicrobial concentrate and use composition comprising an effective microbicidal amount of a C_1–C_4 peroxycarboxylic acid, and an effective microbicidal amount of a C_6–C_{18} peroxyacid. We have found that combining these acids produces a synergistic effect, producing a much more potent biocide than can be obtained by using these components separately. The concentrate composition can be diluted with a major proportion of water to form an antimicrobial sanitizing use solution having a pH in the range of about 2 to 8. The sanitizing use solution can be used effectively to clean or sanitize facilities and equipment used in the food processing, food service and health care industries.

PERACIDS

The present invention is based upon the surprising discovery that when a C_6–C_{18} peroxyacid is combined with a C_1–C_4 peroxycarboxylic acid, a synergistic effect is produced and greatly enhanced antimicrobial activity is exhibited when compared to the C_6–C_{18} peroxyacid or the C_1–C_4 peroxycarboxylic acid alone. The present blend of a C_6–C_{18} peroxyacid and a C_1–C_4 peroxycar-

boxylic acid can effectively kill microorganisms (e.g., a 5 $\log_{10}$ reduction in 30 seconds) from a concentration level below 100 ppm and as low as 20 ppm of the peracid blend.

A variety of C_6–C_{18} peroxyacids may be employed in the composition of the invention such as peroxyfatty acids, monoperoxy- or diperoxydicarboxylic acids, and peroxyaromatic acids. The C_6–C_{18} peroxyacids employed in the present invention may be structurally represented as follows: R_1—CO_3H, wherein R_1 is a hydrocarbon moiety having from about 5 to 17 carbon atoms (a C_{18} peroxyacid is generally represented structurally as C_7—CO_3H). R_1 may have substituents in the chain, e.g., —OH, CO_2H, or heteroatoms (e.g., —O—as in alkylether carboxylic acids), as long as the antimicrobial properties of the overall composition are not significantly affected. It should be recognized that "R_1" substituents or heteroatoms may change the overall acidity (i.e., pKa) of the carboxylic acids herein described. Such modification is within the contemplation of the present invention provided the advantageous antimicrobial performance is maintained. Furthermore, R_1 may be linear, branched, cyclic or aromatic. Preferred hydrocarbon moieties (i.e. preferred R_1's) include linear, saturated, hydrocarbon aliphatic moieties having from 7 to 11 carbon atoms (or 8 to 12 carbon atoms per molecule).

Specific examples of suitable C_6–C_{18} carboxylic fatty acids which can be reacted with hydrogen peroxide to form peroxyfatty acids include such saturated fatty acids as hexanoic (C_6), enanthic (heptanoic) (C_7), caprylic (octanoic) (C_8), pelargonic (nonanoic) (C_9), capric (decanoic) (C_{10}), undecyclic (undecanoic) (C_{11}), lauric (dodecanoic) (C_{12}), trideclic (tridecanoic) (C_{13}), myristic (tetradecanoic) (C_{14}), palmitic (hexadecanoic) (C_{16}), and stearic (octodecanoic) (C_{18}). These acids can be derived from both natural and synthetic sources. Natural sources include animal and vegetable fats or oils which should be fully hydrogenated. Synthetic acids ca be produced by the oxidation of petroleum wax. Particularly preferred peroxyfatty acids for use in the composition of the invention are linear monoperoxy aliphatic fatty acids such as peroxyoctanoic acid, peroxydecanoic acid, or mixtures thereof.

Other suitable C_6–C_{18} peroxyacids are derived from the oxidation of dicarboxylic acids and aromatic acids. Suitable dicarboxylic acids include adipic acid (C_6) and sebacic acid (C_{10}). An example of a suitable aromatic acid is benzoic acid. These acids can be reacted with hydrogen peroxide to form the peracid form suitable for use in the composition of the invention. Preferred peracids in this group include monoperoxy- or diperoxyadipic acid, monoperoxy- or diperoxysebacic acid, and peroxybenzoic acid.

The above peroxyacids provide antibacterial activity against a wide variety of microorganisms, such as gram positive (e.g., *Staphylococcus aureus*) and gram negative (e.g., *Escherichia coli*) microorganisms, yeast, molds, bacterial spores, etc. When the above C_6–C_{18} peroxyacids are combined with a C_1–C_4 peroxycarboxylic acid, greatly enhanced activity is shown compared to the C_1–C_4 peroxycarboxylic acid alone or the C_6–C_{18} peroxyacid alone. The C_1–C_4 peroxycarboxylic acid component can be derived from a C_1–C_4 carboxylic acid or dicarboxylic acid by reacting the acid with hydrogen peroxide. Examples of suitable C_1–C_4 carboxylic acids include acetic acid, propionic acid, glycolic acid, and succinic acid. Preferable C_1–C_4 peroxycarboxylic acids for use in the composition of the invention include peroxyacetic acid, peroxypropionic acid, peroxyglycolic acid, peroxysuccinic acid, or mixtures thereof.

The antimicrobial concentrate of the present invention can comprise about 0.01 to 10 wt. %, preferably about 0.05 to 5 wt. %, and most preferably about 0.1 to 2 wt. % of a C_6–C_{18} peroxyacid, and about 0.1 to 25 wt. %, preferably about 0.5 to 20 wt. %, and most preferably about 1 to 15 wt. % of a C_1–C_4 peroxycarboxylic acid. The concentrate composition preferably has a weight ratio of C_1–C_4 peroxycarboxylic acid to C_6–C_{18} peroxyacid of about 15:1 to 3:1. The concentrate contains sufficient acid so that the end use solution has a pH of about 2 to 8, preferably about 3 to 7. Some acidity may come from an inert acidulant which may be optionally added (e.g., phosphoric acid).

The peracid components used in the composition of the invention can be produced in a simple manner by mixing a hydrogen peroxide (H_2O_2) solution with the desired amount of acid. With the higher molecular weight fatty acids, a hydrotrope coupler may be required to help solubilize the fatty acid. The H_2O_2 solution also can be added to previously made peracids such as peracetic acid or various perfatty acids to produce the peracid composition of the invention. The concentrate can contain about 1 to 50 wt. %, preferably about 5 to 25 wt. % of hydrogen peroxide.

The concentrate composition can further comprise a free C_6–C_{18} carboxylic acid, a free C_1–C_4 carboxylic acid, or mixtures thereof. The free acids will preferably correspond to the starting materials used in the preparation of the peroxyacid components. The free C_6–C_{18} carboxylic acid is preferably linear and saturated, has 8 to 12 carbon atoms per molecule, and can also comprise a mixture of acids. The free C_6–C_{18} carboxylic acid and free C_1–C_4 carboxylic acid can be present as a result of an equilibrium reaction with the hydrogen peroxide to form the peroxyacids.

OPTIONAL COMPONENTS

Various optional materials may be added to the composition of the invention to help solubilize the fatty acids, restrict or enhance the formation of foam, to control hard water, to stabilize the composition, or to further enhance the antimicrobial activity of the composition.

The composition of the invention can contain a surfactant hydrotrope coupling agent or solubilizer that permits blending short chain perfatty acids in aqueous liquids. Functionally speaking, the suitable couplers which can be employed are non-toxic and retain the fatty acid and the perfatty acid in aqueous solution throughout the temperature range and concentration to which a concentrate or any use solution is exposed.

Any hydrotrope coupler may be used provided it does not react with the other components of the composition or negatively affect the antimicrobial properties of the composition. Representative classes of hydrotropic coupling agents or solubilizers which can be employed include anionic surfactants such as alkyl sulfates and alkane sulfonates, linear alkyl benzene or naphthalene sulfonates, secondary alkane sulfonates, alkyl ether sulfates or sulfonates, alkyl phosphates or phosphonates, dialkyl sulfosuccinic acid esters, sugar esters (e.g., sorbitan esters) and C_8–C_{10} alkyl glucosides. Preferred coupling agents for use in the present invention include n-octanesulfonate, available as NAS 8D from Ecolab,

and the commonly available aromatic sulfonates such as the alkyl benzene sulfonates (e.g. xylene sulfonates) or naphthalene sulfonates.

Some of the above hydrotropic coupling agents independently exhibit antimicrobial activity at low pH. This adds to the efficacy of the present invention, but is not the primary criterion used in selecting an appropriate coupling agent. Since it is the presence of perfatty acid in the protonated neutral state which provides biocidal activity, the coupling agent should be selected not for its independent antimicrobial activity but for its ability to provide effective interaction between the substantially insoluble perfatty acids described herein and the microorganisms which the present compositions control.

The hydrotrope coupling agent can comprise about 0.1 to 30 wt. %, preferably about 1 to 20 wt. %, and most preferably about 2 to 15 wt. % of the concentrate composition.

Compounds such as mono, di and trialkyl phosphate esters may be added to the composition to suppress foam. Such phosphate esters would generally be produced from aliphatic linear alcohols, there being from 8 to 12 carbon atoms in the aliphatic portions of the alkyl phosphate esters. Alkyl phosphate esters possess some antimicrobial activity in their own right under the conditions of the present invention. This antimicrobial activity also tends to add to the overall antimicrobial activity of the present compositions even though the phosphate esters may be added for other reasons. Furthermore, the addition of nonionic surfactants would tend to reduce foam formation herein. Such materials tend to enhance performance of the other components of the composition, particularly in cold or soft water. A particularly useful nonionic surfactant for use as a defoamer is nonylphenol having an average of 12 moles of ethylene oxide condensed thereon, it being encapped with a hydrophobic portion comprising an average of 30 moles of propylene oxide.

Chelating agents can be added to the composition of the invention to enhance biological activity, cleaning performance and stability of the peroxyacids. For example, 1-hydroxyethylidene-1,1-diphosphonic acid commercially available from the Monsanto Company under the designation "DEQUEST" has been found to be effective. Chelating agents can be added to the present composition to control or sequester hardness ions such as calcium and magnesium. In this manner both detergency and sanitization capability can be enhanced.

Other materials which are sufficiently stable at the low pH contemplated by the present composition may be added to the composition to impart desirable qualities depending upon the intended ultimate use. For example, phosphoric acid (H_3PO_4) can be added to the composition of the invention. Additional compounds can be added to the concentrate (and thus ultimately to the use solution) to change its color or odor, to adjust its viscosity, to enhance its thermal (i.e., freeze-thaw) stability or to provide other qualities which tend to make it more marketable.

The composition of the invention can be made by combining by simple mixing an effective amount of a C_6–C_{18} peroxyacid such as a peroxyfatty acid with some source of a C_1–C_4 peroxycarboxylic acid such as peroxyacetic acid. This composition would be formulated with preformed perfatty acid and preformed peroxyacetic acid. A preferred composition of the invention can be made by mixing a C_1–C_4 carboxylic acid, a C_6–C_{18} carboxylic acid, a coupler and a stabilizer and reacting this mixture with hydrogen peroxide. A stable equilibrium mixture is produced containing a C_1–C_4 peroxycarboxylic acid and a C_6–C_{18} peroxyacid by allowing the mixture to stand for from one to seven days at 15° C. to 25° C. As with any aqueous reaction of hydrogen peroxide with a free carboxylic acid, this gives a true equilibrium mixture. In this case, the equilibrium mixture will contain hydrogen peroxide, a C_1–C_4 carboxylic acid, a C_6–C_{18} carboxylic acid, a C_1–C_4 peroxycarboxylic acid, a C_6–C_{18} peroxyacid, water, and various couplers and stabilizers.

By using the above approach, the composition of the invention can be formulated by merely mixing readily available raw materials, e.g., acetic acid, hydrogen peroxide and fatty acid. By allowing solution time for equilibrium to be obtained, the product containing both of the active biocides is obtained. In varying the ratio of C_1–C_4 carboxylic acid to C_6–C_{18} carboxylic acid, it is easy to vary the ratio of C_1–C_4 peroxycarboxylic acid to C_6–C_{18} peroxyacid.

CONCENTRATE AND USE COMPOSITIONS

The present invention contemplates a concentrate composition which is diluted to a use solution prior to its utilization as a sanitizer. Primarily for reasons of economics, the concentrate would normally be marketed and the end user would dilute the concentrate with water to a use solution. A preferred antimicrobial concentrate composition comprises about 0.01 to 10 wt. %, preferably about 0.05 to 5 wt. %, of a C_6–C_{18} peroxyfatty acid, about 0.1 to 25 wt. %, preferably about 0.5 to 20 wt. %, of a C_1–C_4 peroxycarboxylic acid, about 0.1 to 30 wt. % of a hydrotrope coupling agent, and about 1 to 50 wt. % of hydrogen peroxide. Other acidulants may optionally be employed in the composition such as phosphoric acid.

The level of active components in the concentrate composition is dependent upon the intended dilution factor and desired acidity in the use solution. The C_6–C_{18} peroxyacid component is generally obtained by reacting a C_6–C_{18} carboxylic acid with hydrogen peroxide in the presence of a C_1–C_4 carboxylic acid. The resulting concentrate is diluted with water to provide the use solution. Generally, a dilution of 1 fluid oz. to 4 gallons (i.e. dilution of 1 to 500 by volume) or to 8 gallons (i.e. dilution of 1 to 1,000 by volume) of water can be obtained with 2% to 20% total peracids in the concentrate. Higher use dilution can be employed if elevated use temperature (greater than 20° C.) or extended exposure time (greater than 30 seconds) are also employed.

In its intended end use, the concentrate is diluted with a major proportion of water and used for purposes of sanitization. The typical concentrate composition described above is diluted with available tap or service water to a formulation of approximately 1 oz. concentrate to 8 gallons of water. An aqueous antimicrobial sanitizing use solution comprises at least about 1 part per million (ppm), preferably about 2 to 10 ppm of a C_6–C_{18} peroxyacid, and at least about 10 ppm, preferably about 20 to 50 ppm of a C_1–C_4 peroxycarboxylic acid. The weight ratio of C_6–C_{18} peroxyacid to C_1–C_4 peroxycarboxylic acid ranges from about 0.01 to 0.5 parts, preferably about 0.02 to 0.2 parts of C_6–C_{18} peroxyacid per part of C_1–C_4 peroxycarboxylic acid. Preferably the total peracid concentration in the use solution is less than about 75 ppm, and most preferably

between about 5 to 50 ppm. Higher levels of peracids can be employed in the use solution to obtain disinfecting or sterilizing results.

The aqueous use solution can further comprise at least about 1 ppm, preferably about 2 to 20 ppm, of a hydrotrope coupling agent, at least about 1 ppm, preferably about 2 to 200 ppm of hydrogen peroxide, and at least about 1 ppm, preferably about 2 to 200 ppm of a free C_6–C_{18} carboxylic acid, a free C_1–C_4 carboxylic acid, or mixtures thereof. The aqueous use solution has a pH in the range of about 2 to 8, preferably about 3 to 7.

METHODS OF USE

As noted above, the present composition is useful in the cleaning or sanitizing of processing facilities or equipment in the food service, food processing or health care industries. Examples of process facilities in which the composition of the invention can be employed include a milk line dairy, a continuous brewing system, food processing lines such as pumpable food systems and beverage lines, etc. Food service wares can also be disinfected with the composition of the invention. The composition is also useful in sanitizing or disinfecting solid surfaces such as floors, counters, furniture, medical tools and equipment, etc., found in the health care industry. Such surfaces often become contaminated with liquid body spills such as blood, other hazardous body fluids or mixtures thereof.

Generally, the actual cleaning of the in-place system or other surface (i.e., removal of unwanted offal therein) is accomplished with a different material such as a formulated detergent which is introduced with heated water. After this cleaning step, the instant sanitizing composition would be applied or introduced into the system at a use solution concentration in unheated, ambient temperature water. The present sanitizing composition is found to remain in solution in cold (e.g., 40° F./4° C.) water and heated (e.g., 140° F./60° C.) water. Although it is not normally necessary to heat the aqueous use solution of the present composition, under some circumstances heating may be desirable to further enhance its antimicrobial activity.

A method of sanitizing substantially fixed in-place process facilities comprises the following steps. The use composition of the invention is introduced into the process facilities at a temperature in the range of about 4° to 60° C. After introduction of the use solution, the solution is circulated throughout the system for a time sufficient to sanitize the process facilities (i.e., to kill undesirable microorganisms). After the system has been sanitized by means of the present composition, the use solution is drained from the system. Upon completion of the sanitizing step, the system optionally may be rinsed with other materials such as potable water. The composition is preferably circulated through the process facilities for 10 minutes or less.

The composition may also be employed by dipping food processing equipment into the use solution, soaking the equipment for a time sufficient to sanitize the equipment, and wiping or draining excess solution off the equipment. The composition may be further employed by spraying or wiping food processing surfaces with the use solution, keeping the surfaces wet for a time sufficient to sanitize the surfaces, and removing excess solution by wiping, draining vertically, vacuuming, etc.

The composition of the invention may also be used in a method of sanitizing hard surfaces such as institutional type equipment, utensils, dishes, health care equipment or tools, and other hard surfaces. The composition may also be employed in sanitizing clothing items or fabric which have become contaminated. The use composition is contacted with any of the above contaminated surfaces or items at use temperatures in the range of about 4° to 60° C., for a period of time effective to sanitize, disinfect, or sterilize the surface or item. For example, the concentrate composition can be injected into the wash or rinse water of a laundry machine and contacted with contaminated fabric for a time sufficient to sanitize the fabric. Excess solution can then be removed by rinsing or centrifuging the fabric.

As the term "sanitizing" is used in the method of the instant invention, it means a reduction in the population numbers of undesirable microorganisms by about 5 powers of 10 or greater (i.e., at least 5 orders of magnitude) after a 30 second exposure time. It is to be emphasized that the instant use solution provides cleaning as well as sanitizing performance although its primary utility is sanitizing. The composition may also be used to achieve disinfection or sterilization (i.e., elimination of all microorganisms) by employing higher levels of peracids in the use solution.

The following Examples are intended to illustrate the above invention and should not be construed as to narrow its scope. One skilled in the art will readily recognize that these Examples suggest many other ways in which the present invention could be practiced.

EXAMPLE 1

Experiments were conducted to determine the antimicrobial efficacy of pure peroxyacids. Table I below demonstrates the antimicrobial efficacy of pure peroxyacids at very low levels when exposed to *S. aureus* and *E. coli*. The peroxyacids listed in Table I were tested by diluting them in 0.05M citrate buffer made in distilled water and were exposed to the bacteria for 30 seconds at 20° C. As Table I indicates, the diperoxyacids were somewhat less active than the peroxyfatty acids. Peroxydecanoic acid was very effective at very low levels against *S. aureus*, but higher levels were required to be effective against *E. coli*. Higher levels were also required at pH 5.

TABLE I

Comparison of Cidal Activity of Peroxyacids

Peroxyacid	pH	Minimum concentration required for 5-log reduction (ppm)[a]	
		S. aureus	*E. coli*
Peroxyhexanoic (C_6)	3.5	15	15
	5.0	20	15
Diperoxyadipic (C_6)	3.5	>50	40
	5.0	>60	35
Peroxyoctanoic (C_8)	3.5	5	5
	5.0	10	15
Peroxydecanoic (C_{10})	3.5	3	10
	5.0	1	30
Diperoxysebacic (C_{10})	3.5	15	15
	5.0	10	50

[a]Peroxyacids tested at 5-ppm increments, or at 1, 3, and 5 ppm where appropriate.

In Table II below, the antimicrobial synergism between the C_2 and C_3 peroxyacids when combined with C_8 and C_{10} peroxyfatty acids is shown. As Table II shows, there was little or no antimicrobial activity when the C_2 and C_3 peroxyacids and the C_8 and C_{10} peroxyfatty acids were tested alone. However, when a

C_2 or C_3 peroxyacid was combined with a C_8 or C_{10} peroxyfatty acid, the bacterial kill of *E. coli* multiplied exponentially. These tests were conducted at pH 4.5 or 5, the pH at which *E. coli* is more difficult to kill (see Table II).

TABLE II

Synergistic Interaction of Peroxyacids				
C_2 [Peroxyacetic] (ppm)	C_3 [Peroxypropionic] (ppm)	C_8 [Peroxyoctanoic] (ppm)	C_{10} [Peroxydecanoic] (ppm)	Log reduction
25		0		0[a]
0		5		0.1[a]
25		5		3.8[a]
	25	0		0.3[b]
	0	6		0.1[b]
	25	6		3.9[b]
30			0	0.7[a]
0			6	0[a]
30			6	2.6[a]

[a]*E. coli*, pH 5, distilled water
[b]*E. coli*, pH 4.5, 500 ppm hard water

EXAMPLE 2

A mixture of short chain fatty acids commercially available from Emery Corporation under the designation "EMERY 658" was employed in producing a sanitizing concentrate composition of the present invention. The "EMERY 658" acid is a mixture of caprylic acid (C_8) and capric acid (C_{10}). The perfatty acids were prepared by the method of Parker, et al., *J. Amer. Chem. Soc.*, 77, 4037 (1955) which is incorporated by reference. The perfatty acid component (also containing 34% acetic acid and 10% hydrogen peroxide) was combined with a pre-made solution of 10.42% peracetic acid, a separate amount of acetic acid, water, and an n-octanesulfonate hydrotrope coupler (NAS 8D). The final composition of this Example was as listed in Table III.

EXAMPLE 3

A second composition of the present invention was prepared as described in Example 2, except that caprylic acid (C_8) and capric acid (C_{10}) replaced some of the perfatty acid of Example 2. The concentration of peracetic acid was 5% while the concentration of perfatty acids was reduced to 1.5% (See Table III).

EXAMPLE 4

The composition of Example 4 was prepared according to the procedure of Example 2, except that no peracetic acid or hydrogen peroxide was added to the composition. The acetic acid component was increased to 39 wt. % and the composition contained 5% perfatty acid (see Table III). Also, a chelating agent (Dequest 2010) was added to the composition.

EXAMPLE 5

The composition of Example 5 was prepared the same as Example 4 except that caprylic acid and capric acid were added to the composition in addition to the percaprylic and percapric acid of Example 4. The composition contained 3.5% fatty acid and 1.5% perfatty acid (see Table III).

EXAMPLE 6

Example 6 was prepared with only peracetic acid, acetic acid, hydrogen peroxide, and water. No perfatty acids or fatty acids were added to the composition of Example 6. The concentration of total peracid was about 5% and the acetic acid concentration was about 39% (see Table III).

EXAMPLE 7

Example 7 was prepared the same as Example 5 except that no peracids were employed, only a mixture of fatty acids and acetic acid was used, along with water, NAS 8D, and Dequest 2010. The composition contained 5% fatty acid (see Table III).

TABLE III

Ingredient	Wt % of Ingredients					
	Ex. 2	Ex. 3	Ex. 4	Ex. 5	Ex. 6	Ex. 7
Peracetic Acid (10.42% solution, 34% acetic acid, 10% H_2O_2)	50	50	—	—	50	—
Acetic Acid	22	22	39	39	22	39
Percaprylic Acid (C_8)	3.75	1.125	3.75	1.125	—	—
Percapric Acid (C_{10})	1.25	0.375	1.25	0.375	—	—
Caprylic Acid (C_8)	—	2.625	—	2.625	—	3.75
Capric Acid (C_{10})	—	0.875	—	0.875	—	1.25
NAS 8D	10	10	10	10	—	10
Water	13	13	45	45	28	45
Dequest 2010	—	—	1	1	—	1

ANTIMICROBIAL EFFICACY OF EXAMPLES 2–7

The compositions prepared according to Examples 2–7 were tested for their antimicrobial efficacy using the testing procedure of the standard A.O.A.C. sanitizing test. All of the samples tested of Examples 2–7 were made about 1 hour prior to testing. The bacteria used in the test procedure were *S. aureus* and *E. coli*. Distilled water was used to dilute the concentrate compositions of Examples 2–7 and the composition was employed at room temperature. The following neutralizers were employed in the test: 0.1% thiosulfate, peptone, 0.5% K_2HPO_4, 0.025% catalase for peracetic acid; chambers for fatty acid; 0.1% thiosulfate, peptone, 0.025% catalase for peracetic acid/fatty acid (perfatty acid).

The antimicrobial activity of Examples 2–7 are summarized in Table IV. Examples 2 and 3 were tested using four samples (a,b,c,d) and Examples 4–7 were tested using two samples (a,b). As can be seen in Table IV, Examples 2–5 exhibited excellent kill (>log 6) of both *S. aureus* and *E. coli* at 50 ppm of peracid. Examples 6 and 7 (containing no perfatty acids) exhibited little or no activity. More specifically, Example 2 was tested at 1,000 and 500 ppm total product (50 and 25 ppm of both peroxyacetic acid and perfatty acid). At these low concentrations, the peracid combination gave a 6–7 log reduction in the bacterial count. Example 3 was tested at 1,000 and 500 ppm total product, and also had a 6–7 log reduction in the bacterial count. At the 500 ppm product concentration the product corresponds to 25 ppm of peroxyacetic acid and 7.5 ppm of perfatty acids. Example 4, at 1,000 ppm of total product (50 ppm of perfatty acid), completely killed all bacteria (greater than 7 log reduction). Example 5 also resulted in a complete kill using 1,000 ppm of total product (15 ppm perfatty acid). Example 6 contained no perfatty acid (only 50 ppm of peroxyacetic acid) and showed no

activity against *S. aureus* and poor activity against *E. coli*. This is due to the fact that peroxyacetic acid is generally not effective at this level, and is generally used at concentrations greater than 100 ppm. Example 7, containing 5% fatty acid (30 ppm) and no perfatty acid at 1,000 ppm total product showed no activity toward either organism.

TABLE IV

Ex.	Sample	Test Product Concentration (ppm)	POAA[1]/POFA[2]/FA[3] Concentration (ppm)	pH	Log$_{10}$ Kill *S. aureus*	Log$_{10}$ Kill *E. coli*
2	a	1000	50/50/0	3.5	6.13	>7.30
	b	1000	50/50/0	3.5	6.52	7.30
	c	500	25/25/0	3.68	6.63	7.00
	d	500	25/25/0	3.68	6.78	7.30
3	a	1000	50/15/35	3.52	7.18	7.30
	b	1000	50/15/35	3.52	6.63	6.90
	c	500	25/7.5/17.5	3.68	6.70	6.76
	d	500	25/7.5/17.5	3.68	7.18	7.00
4	a	1000	0/50/0	3.5	>7.18	>7.30
	b	1000	0/50/0	3.5	>7.18	>7.30
5	a	1000	0/15/35	3.5	>7.18	>7.30
	b	1000	0/15/35	3.5	>7.18	>7.30
6	a	1000	50/0/0	3.49	NMA[4]	3.48
	b	1000	50/0/0	3.49	NMA	3.80
7	a	1000	0/0/30	3.46	NMA	NMA
	b	1000	0/0/30	3.46	NMA	NMA

[1]POAA = Peroxyacetic Acid
[2]POFA = Peroxyfatty Acid
[3]FA = Fatty Acid
[4]NMA = No measurable activity

EXAMPLES 8–11

Examples 8–11 were prepared by substantially the same procedure as the previous Examples, except that hydrogen peroxide (H_2O_2) was mixed with acetic acid and C_{8-10} fatty acids (Emery 658) to make the peracids of the composition. Table V summarizes the components and amounts of the various compositions of Examples 8–11 which were made.

TABLE V

Ingredient	Peracid Test Formulations Ex. 8	Ex. 9	Ex. 10	Ex. 11
Acetic Acid	44	39	34	49
H_2O_2 (35%)	40	40	40	40
Dequest 2010	1	1	1	1
NAS 8D	10	10	10	10
Emery 658	5	10	15	—

PERACID STABILITY, CIDAL ACTIVITY OF EXAMPLES 8–11

Each of Examples 8–11 were tested for peracid stability and cidal activity using the A.O.A.C. sanitizing test against *S. aureus* and *E. coli* at room temperature with the formulations diluted in distilled water. Tables VI–IX show the cidal activity of each formulation. Generally all of the formulations reached maximum peracid formation within about 12 days. All of the formulations obtained about 12.5% peracid except Example 10 (15% fatty acid) which obtained about 11.5% peracid.

Table VI summarizes the cidal activity of Example 8 in which the composition was measured for cidal activity on the first day up to day 33. At 250 ppm of total product, there were about 4–5 ppm of perfatty acid and about 20 ppm of peracetic acid as determined by carbon 13 NMR spectroscopy. The results are summarized in Table VI.

TABLE VI

Day	Peracid Percent	Peracid Stability, Cidal Activity of Example 8 Test[a] Concentration	Test pH	Ave. Log Reduction *S. aureus*	Ave. Log Reduction *E. coli*
1	4.28	250 ppm	3.92	6.28	NMA[b]
6	11.00	250 ppm	3.91	>7.38	>7.18
8	11.08	250 ppm	3.86	>7.11	>7.12
12	12.43	250 ppm	3.83	>7.18	6.96
15	12.74	250 ppm	3.88	6.83	—
33	10.18	250 ppm	3.83	5.18	6.34

[a]ppm total product
[b]No measurable activity

The cidal activity of Example 9 is summarized in Table VII below. The peracetic acid concentration at 250 ppm of product was about 20–21 ppm and the concentration of perfatty acid was about 11 ppm. The concentration of peracetic acid at 50 ppm of product was about 4 ppm and the concentration of perfatty acid was about 2 ppm.

TABLE VII

Day	Peracid Percent	Peracid Stability, Cidal Activity of Example 9 Test[a] Concentration	Test pH	Ave. Log Reduction *S. aureus*	Ave. Log Reduction *E. coli*
1	4.88	250 ppm	3.95	>7.60	NMA[b]
6	10.62	250 ppm	3.92	>7.38	>7.18
8	11.61	250 ppm	3.98	>7.11	>7.12
12	12.47	250 ppm	3.91	>7.18	>7.23
15	12.00	250 ppm	3.95	6.95	—
		120 ppm	4.18	>7.13	—
		50 ppm	4.41	6.39	—
33	10.49	250 ppm	3.85	5.20	6.22

[a]ppm total product
[b]No measurable activity

The cidal activity of Example 10 is summarized in Table VIII below. At 250 ppm of product the peracetic acid concentration was about 19 ppm and the perfatty acid concentration was about 14 ppm.

TABLE VIII

Day	Peracid Percent	Peracid Stability, Cidal Activity of Example 10 Test[a] Concentration	Test pH	Ave. Log Reduction *S. aureus*	Ave. Log Reduction *E. coli*
1	4.84	250 ppm	3.90	>7.60	NMA[b],

TABLE VIII-continued

Day	Peracid Percent	Peracid Stability, Cidal Activity of Example 10 Test[a] Concentration	Test pH	Ave. Log Reduction S. aureus	E. coli
					4.04
6	9.81	250 ppm	3.96	>7.38	>7.18
8	10.99	250 ppm	3.96	>7.11	>7.12
12	11.47	250 ppm	3.94	>7.18	>7.23
15	11.48	250 ppm	3.96	6.83	—
33	10.49	250 ppm	3.95	5.25	6.53

[a]ppm total product
[b]No measurable activity

The cidal activity of Example 11 is summarized in Table IX below. At 250 ppm of product there was about 27 ppm of peracetic acid. At 1000 ppm of product there was about 108 ppm of peracetic acid. No fatty acid was employed in the composition of Example 11.

TABLE IX

Day	Peracid Percent	Cidal Activity of Example 11 Test[a] Concentration	Test pH	Ave. Log reduction S. aureus	E. coli
5	10.95	250 ppm	3.90	NMA[b]	NMA
7	12.03	1000 ppm	3.50	4.60	>7.12
11	12.44	1000 ppm	3.49	6.38	6.64
14	12.53	1000 ppm	3.50	4.17	—
32	10.77	1000 ppm	3.45	4.77	6.44

[a]ppm total product
[b]No measurable activity

When comparing the formulations containing fatty acid (Tables VI–VIII), poor activity was measured against *E. coli* one day after being formulated. Since the total peracid values were low, more fatty acid was present and gram negative bacteria tend to be less sensitive than gram positive bacteria to the C_8–C_{10} fatty acids. However, as more peracid developed over the days indicated, increased cidal activity against *E. coli* was observed. Table IX indicates that to obtain acceptable activity (greater than or equal to 5 log reduction) using only peracetic acid, the peracetic acid must be tested over 100 ppm active. Secondly, this oxidizing compound is more effective against *E. coli* than *S. aureus*.

Generally all the formulations containing fatty acid remain stable after about 1 month. This was confirmed by repeated testing over time at 250 ppm total product for each formulation in which greater than 5 log reductions were measured against *S. aureus* and *E. coli*.

EXAMPLES 12–17

The cidal activity of a two-component system containing both peracetic acid and fatty acid was investigated using the A.O.A.C. sanitizing test. Table X shows the product formulations examined. The test samples include controls showing cidal activity of NAS 8D as well as fatty acid kill against *S. aureus*. All the samples were tested in distilled water.

TABLE X

Ingredient	Wt % Ingredient Ex. 12	Ex. 13	Ex. 14	Ex. 15	Ex. 16	Ex. 17
Base 1[a]	80	80	80	80	—	—
Base 2[b]	—	—	—	—	80	80
NAS 8D	10	—	10	10	10	10
Octanoic Acid	—	—	10	—	—	10
Emery 658	—	—	—	10	10	—
H_2O	10	20	—	—	—	—

[a]H_2O_2, 35%; acetic acid, 35%; Dequest 2010, 1%; H_3PO_4 (85%), 29%.
[b]Acetic acid, 35%; Dequest 2010, 1%; H_3PO_4 (85%), 29%; H_2O, 35%.

Table XI shows the activity measurement of each of Examples 12–17 at various test concentrations. When testing the peracetic acid formulation of Examples 12 and 13 (having no fatty acid), biocidal activity occurred only at 100 ppm or greater. Cidal activity (greater than 4 log reduction) was measured at a minimal concentration of 10 ppm peracid with fatty acid in the system (Example 14). At 10 ppm peracid, the composition containing Emery 658 (Example 15) had better activity than the system containing only C_8 (octanoic) fatty acid (Example 14). In the fatty acid controls (Examples 16 and 17), the Emery 658 had more cidal activity than the C_8 fatty acid. At total product test concentrations equivalent to 10 or 25 ppm peracid, the fatty acid in the system of Example 16 did not have significant cidal activity. Example 17 did not have significant cidal activity at any test concentration.

TABLE XI

Example	Peracid Cidal Activity Against S. aureus Peracid (%)	Concentration (ppm Peracid)	Test pH	Log[a] Reduction
12	7.02	50	2.79	NMA[b]
		100	2.54	5.45
		150	2.41	>7.70
13	6.25	50	2.76	NMA
		100	2.52	4.51
		150	2.40	5.84
14	9.32	10	3.52	4.22
		25	3.16	>7.70
		50	2.90	>7.70
15	9.73	10	3.50	6.82
		25	3.19	7.55
		50	2.88	>7.70
16	—	—[c]	3.53	0.70
		—[c-1]	3.18	1.04
		—[c-2]	2.88	4.07
17	—	—[d]	3.51	0.93
		—[d-1]	—	0.66
		—[d-2]	—	0.97

[a]Average of duplicate testing.
[b]No measurable activity.
[c]Same total product concentration as Example 15 @ 10 ppm peracid (about 100 ppm product).
[c-1]Same total product concentration as Example 15 @ 25 ppm peracid (about 250 ppm product).
[c-2]Same total product concentration as Example 15 @ 50 ppm peracid (about 500 ppm product).
[d]Same total product concentration as Example 14 @ 10 ppm peracid (about 100 ppm product).
[d-1]Same total product concentration as Example 14 @ 25 ppm peracid (about 250 ppm product).
[d-2]Same total product concentration as Example 14 @ 50 ppm peracid (about 500 ppm product).

The cidal activity of a peracetic acid/fatty acid system was measured comparing freshly made formulations to month-old formulations of Examples 14 and 15. These formulations are shown in Table XII which compares the titration values of month-old formulations to the same freshly prepared. Table XIII shows the cidal activity of month-old and fresh formulations of Examples 14 and 15.

TABLE XII

	Peracid Titration Values Ex. 14	Ex. 15	Ex. 14	Ex. 15
Date formulated	Month-Old	Month-Old	Fresh	Fresh

TABLE XII-continued

	Peracid Titration Values			
	Ex. 14	Ex. 15	Ex. 14	Ex. 15
% H_2O_2	2.15	2.07	1.99	1.99
% Peracid	5.37	5.35	4.85	4.86
% Total O_2	2.14	2.10	1.96	1.96

TABLE XIII

	Peracid Cidal Activity Against *S. aureus*			
Example	Peracid (%)	Test Concentration (ppm Peracid)	Test pH	Log[a] Reduction
14	5.37	10	3.46	NMA[b]
(Month-Old)		25	3.07	>7.48
14	4.85	10	3.34	5.07
(Fresh)		25	2.97	7.30
15	5.35	10	3.52	5.29
(Month-Old)		25	3.04	7.24
15	4.86	10	3.42	NMA[c]/ 3.68
(Fresh)		25	2.99	7.48

[a]Average of duplicate testing.
[b]No measurable activity.
[c]Duplicate testing in which only one sample exhibited cidal activity.

As can be seen from Table XIII, cidal activity in the peracetic acid/fatty acid system occurs at test concentrations as low as 10 or 25 ppm peracid. Mixed results occurred at 10 ppm peracid between the month-old and fresh formulations of Examples 14 and 15, however, increasing the concentration to 25 ppm resulted in a uniform kill activity (>7 log reduction).

An additional test was run to determine how quickly compounds exhibiting cidal activity are formed upon adding fatty acid to a peracetic acid system. Examples 12, 15 and 16 were tested. Examples 12 and 15 were formulated the day before testing and were day-old samples. Another test sample of Example 15 was formulated immediately prior to testing. Example 16 containing Base 2 (no H_2O_2) was used to show cidal activity from the fatty acid at low test concentrations. Table XIV shows the cidal activity of each Example in distilled water against *S. aureus*.

TABLE XIV

	Cidal Activity Against *S. aureus*			
Example	Age	ppm Peracid	Test pH	Log[a] Reduction
12	1 day	50	2.94	NMA[b]
		100	2.71	6.60
15	1 day	10	3.68	7.02
		25	3.35	>7.20
15	fresh	10	3.76	NMA
		25	3.32	NMA
16	22 days	—[c]	3.74	NMA
		—[d]	—	NMA

[a]Average of duplicate testing.
[b]No measurable activity.
[c]Equivalent total product concentration as Example 15 (day old) @ 10 ppm peracid.
[d]Equivalent total product concentration as Example 15 (day old) @ 25 ppm peracid.

The data from Table XIV suggests that the formation of compounds containing cidal activity when adding fatty acid to a peracetic acid system is not immediate, but does occur within a day. The formation of compounds exhibiting cidal activity occurred within a day after adding fatty acid to the peracetic acid system as in Example 15 with cidal activity occurring at a concentration as low as 10 ppm peracid. Thus, the cidal activity is not due to the mere combination of fatty acid and peroxyacetic acid, but the fatty acid must be converted to the perfatty acid before substantially enhanced cidal activity occurs.

EXAMPLES 18–22

A two-component system containing peracetic acid and perfatty acid was formulated and tested to determine its sanitizing activity over just a peracetic acid system. Table XV shows premixes 1 and 2 used in making the composition. The premixes were both made with H_2O_2 (35% solution), acetic acid, Dequest 2010, and with/without H_3PO_4. Premix 1 was made about 5 months before premix 2. To each premix was added NAS 8D, a C_8 fatty acid or Emery 658 as shown in Table XVI to complete the formulation of Examples 18–21. Example 22 was formulated as a control and had no fatty acid.

TABLE XV

	Peracid Premixes	
	Wt % Component	
Component	Premix 1	Premix 2
H_2O_2 (35%)	75.0	35.0
Acetic acid (glacial)	24.0	35.0
Dequest 2010	1.0	1.0
H_3PO_4 (85%)	—	29.0

TABLE XVI

	Perfatty Acid/Peracetic Acid Formulations				
	Wt % Ingredient				
Ingredient	Ex. 18	Ex. 19	Ex. 20	Ex. 21	(Control) Ex. 22
Premix 1	80.0	—	80.0	—	—
Premix 2	—	80.0	—	80.0	—
NAS 8D	10.0	10.0	10.0	10.0	—
C_8 Fatty Acid	10.0	10.0	—	—	—
Emery 658	—	—	10.0	10.0	—
Acetic Acid (Glacial)	—	—	—	—	24.0
H_2O_2 (35%)	—	—	—	—	75.0
Dequest 2010	—	—	—	—	1.0

Table XVII shows the sanitizing activity measured from each formulation of Examples 18–22 at 50, 100, or 150 ppm peracetic acid against *S. aureus*.

TABLE XVII

	Sanitizing Efficacy of Perfatty Acid/ Peracetic Acid System vs. Sanitizing Efficacy of Peracetic Acid System				
Example	Total Peracid[a] (Percent)	Fatty Acid (Percent)	Test Concentration (ppm)	Test pH	Log[b] Reduction
18	7.69	10.0	150	3.53	>7.06
			100	3.64	>7.06
			50	3.83	>7.06
19	11.21	10.0	150	2.71	>7.06
			100	2.80	>7.06
			50	3.08	>7.06
20	9.08	10.0	150	3.64	>7.06
			100	3.65	>7.06
			50	3.85	>7.06
21	10.92	10.0	150	2.68	>7.06
			100	2.77	>7.06
			50	3.10	>7.06
22	10.40	—	150	3.56	7.06
(Control)			100	3.68	3.89
			50	3.93	NMA[c]

[a]As peracetic acid
[b]Average of duplicate testing against *S. aureus*.
[c]No measurable activity.

Extremely good kill (>7 log reduction) was obtained with or without H_3PO_4 in the perfatty acid formulations of Examples 18–21. The two component system of C_8 fatty acid or Emery 658 in combination with peracetic acid (Examples 18–21) had significantly better kill than the peracetic acid system alone (Example 22) at a test concentration of 50 to 100 ppm. No activity was measured at 50 ppm with the single peracetic acid system of Example 22.

EXAMPLES 23–26

The effect of alkyl chain length on antimicrobial efficacy of perfatty acids was determined for percaprylic (C_8) acid, percapric (C_{10}) acid and a percaprylic/-percapric (3:1) perfatty acid mixture using the compositions of Examples 23–26 summarized in Table XVIII below.

TABLE XVIII

Ingredient	Wt % of Ingredient Ex. 23	Ex. 24	Ex. 25	Ex. 26
Percaprylic (C_8) Acid	1	—	—	—
Percapric (C_{10}) Acid	—	1	—	—
$C_8 + C_{10}$ (3:1) Perfatty Acid	—	—	1	—
Acetic Acid	10	10	10	10
Water	84	84	84	85
NAS 8D	5	5	5	5

The antimicrobial efficacy of Examples 23–26 are summarized in Table XIX below. Examples 23–25 were tested using three samples (a, b, c) of 5, 10, and 15 ppm of perfatty acid respectively. Example 26, containing no perfatty acid, was diluted to an equivalent formulation of Examples 23–25 containing perfatty acid. As can be seen from Table XIX, significant kill occurred at 5 ppm for *S. aureus* using Examples 23–25. Significant kill occurred against *E. coli* at 10 ppm of perfatty acid in Examples 23–25. Example 26 (having no perfatty acid) did not produce any kill of either microorganism.

TABLE XIX

Antimicrobial Efficacy of Examples 23–26

Example	Sample	Perfatty Acid Concentration (ppm)	Log Kill *S. aureus*	Log Kill *E. coli*
23	a	5	>7.0	3.6
	b	10	—	>7.2
	c	15	—	>7.2
24	a	5	>7.0	3.0
	b	10	—	>7.2
	c	15	—	>7.2
25	a	5	>7.0	<3.0
	b	10	—	>7.2, 5.5
	c	15	—	>7.2
26	a	—[a]	0	—
	b	—[b]	—	0

[a]Equivalent total product concentration as Examples 23, 24, 25 at 5 ppm perfatty acid.
[b]Equivalent total product concentration as Examples 23, 24, 25 at 15 ppm perfatty acid.

EXAMPLE 27

The antimicrobial activity of percaprylic acid against *E. coli* was measured at a 30 second exposure at varying pH's. The formulation contained 94% water, 5% NAS 8D, and 1% percaprylic acid. The formulation was diluted in a buffer of 0.05M citrate and 0.05M potassium phosphate. The log kill of this formulation at increasing pH's is summarized in Table XX. Samples containing 7 ppm and 25 ppm of percaprylic acid were tested. As Table XX indicates, significant kill at 7 ppm occurred at a pH of 3.0. Significant kill levels were maintained at 25 ppm through a pH of 7.0.

TABLE XX

Antimicrobial Efficacy of Percaprylic Acid against *E. coli*

pH	Log Kill (Perfatty Concentration 7 ppm)	Log Kill (Perfatty Concentration 25 ppm)
3.0	>7.2	>7.2
5.0	<3.0	>7.2
7.0	<3.0	>7.2
8.9	—	<3.0
9.0	<3.0	—

EXAMPLES 28–30

The compositions of Examples 28–30 were made to determine the limitations on cidal activity of compositions containing at least 30% acetic acid. Higher acetic acid formulations were also tested for their cidal activity. The composition of Example 30 was prepared with no coupler (NAS 8D). The compositional ingredients of Examples 28–30 are summarized below in Table XXI.

TABLE XXI

Ingredient	Wt % of Ingredient Example 28	Example 29	Example 30
Acetic Acid	30.0	50.0	50.0
H_2O_2 (35%)	30.0	15.0	15.0
Dequest 2010	1.0	1.0	1.0
C_8 Fatty Acid	4.0	6.0	5.0
NAS 8D (Spray Dried	5.0	5.0	—
Distilled Water	30.0	23.0	29.0

The antimicrobial efficacy of Examples 28–30 was determined using the procedure of the standard A.O.A.C. sanitizing test. The compositions of Examples 28–30 were diluted with 500 ppm hard water and employed at 25° C. The bacteria used in the test procedure were *S. aureus* and *E. coli*, and a TGE plating medium was employed. Exposure time of the compositions to the bacteria was 30 seconds. The neutralizer employed in the testing procedure contained 0.1% thiosulfate, 1.0% peptone, and 0.025% catalase. The antimicrobial activity of Examples 28–30 is summarized in Table XXII below.

TABLE XXII

Cidal Activity of Examples 28–30

Formulation	Concentration	pH	Log Reduction *S. aureus*	*E. coli*
Example 28	1 oz:8 gal.[a]	4.48	>7.15	>6.89
	1 oz:10 gal.[b]	4.83	>7.15	>6.89
	1 oz:12 gal.[c]	5.04	>7.15	6.41
	1 oz:14 gal.[d]	5.52	>7.15	5.76
	1 oz:16 gal.[e]	5.94	>7.15	2.95
Example 29	40 ppm Active	4.16	>7.15	>6.89
Example 30	40 ppm Active	4.04	>7.15	>6.89

[a]54.2 ppm peracid
[b]43.3 ppm peracid
[c]36.1 ppm peracid
[d]31.0 ppm peracid
[e]27.2 ppm peracid

As Table XXII indicates, very low concentrations of combinations of peroxyacetic acid and peroxyfatty acid are very effective in killing bacteria. Also, Example 30 showed that the composition of the invention is antimicrobially effective without a hydrotrope coupler.

The foregoing discussion and Examples are illustrative of the invention. However, since many embodiments of the invention can be made without departing from the spirit and scope of the invention, the invention resides wholly in the claims hereinafter appended.

I claim:

1. A peroxyacid antimicrobial concentrate composition comprising:

(a) about 0.01 to 25 wt. % of a C_1–C_4 peroxycarboxylic acid;

(b) about 0.01 to 10 wt. % of a peroxyacid of the structure R_1—CO_3H, wherein R_1 comprises a linear, saturated hydrocarbon chain having about 5 to 17 carbon atoms;

(c) about 0.1 to 30 wt. % of a hydrotrope coupling agent capable of solubilizing said peroxyacid of (b) in the concentrate and when the concentrate is diluted with water; and

(d) about 1 to 50 wt. % of hydrogen peroxide; wherein the concentrate composition is capable of being diluted with a major proportion of water to form an antimicrobial sanitizing use solution having a pH in the range of about 3 to 7.

2. The concentrate composition of claim 1 wherein said C_1–C_4 peroxycarboxylic acid comprises peroxyacetic acid, peroxypropionic acid, peroxysuccinic acid, peroxyglycolic acid, or mixtures thereof.

3. The concentrate composition of claim 1 wherein said peroxyacid of (b) is a peroxyfatty acid having about 8 to 12 carbon atoms per molecule.

4. The concentrate composition of claim 3 wherein said peroxyfatty acid comprises peroxyoctanoic acid, peroxydecanoic acid, or mixtures thereof.

5. The concentrate composition of claim 3 wherein the weight ratio of C_1–C_4 peroxycarboxylic acid to peroxyfatty acid is about 15:1 to 3:1.

6. The concentrate composition of claim 1 wherein said hydrotrope comprises n-octanesulfonate.

7. The concentrate composition of claim 3 further comprising about 5 to 50 wt. % of a fatty acid, a C_1–C_4 carboxylic acid, or mixtures thereof.

8. The concentrate composition of claim 7 wherein said C_1–C_4 carboxylic acid component comprises acetic acid, propionic acid, or mixtures thereof.

9. The concentrate composition of claim 7 wherein said fatty acid comprises octanoic acid, decanoic acid, or molecule.

10. The composition of claim 1 further comprising an effective amount of a chelating agent for binding polyvalent metal cations.

11. The composition of claim 10 wherein said chelating agent is 1-hydroxyethylidene-1,1-diphosphonic acid.

12. The composition of claim 11 wherein said chelating agent is present in an amount of about 1 wt. % based on the concentrate composition.

* * * * *

UNITED STATES PATENT AND TRADEMARK OFFICE

CERTIFICATE OF CORRECTION

PATENT NO. : 5,200,189

DATED : April 6, 1993

INVENTOR(S) : Thomas R. Oakes, Patricia M. Stanley and Jerome D. Keller

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

In Column 20, Claim 9, line 20, "molecule" should read

--mixtures thereof--.

Signed and Sealed this

Fourteenth Day of February, 1995

Attest:

BRUCE LEHMAN

Attesting Officer

Commissioner of Patents and Trademarks

Marination to Improve Functional Properties and Safety of Poultry Meat

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Primary Audience: Poultry Processors, Further Processors

SUMMARY

The most commonly used poultry marinades include salt and sodium tripolyphosphate, which have been shown to increase meat yield and water-holding capacity, as well as improve color and texture. Recently, several poultry further-processing facilities have begun using more acidic (pH ~4) type marinades such as sodium lactate, sodium citrate, and sodium diacetate (alone or in combination) to combat the growth of *Listeria monocytogenes* in further-processed meat loaves. Because the acidic marinades currently used in turkey further-processing have a low pH (~4) compared with the previously used salt and sodium tripolyphosphate (~pH 9), these marinades may cause meat quality problems. This review paper will discuss aspects of poultry food safety and meat quality and how acidic marinades can be used to improve safety, specifically by controlling *L. monocytogenes* growth, and how they affect quality of the meat products. Current industry practices will be discussed and reviewed.

Key words: acid marinade, poultry meat, functionality, *Listeria monocytogenes*

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MARINATION

Traditionally, meat has been marinated to improve flavor, improve tenderness, and increase product shelf life. An important aspect of marination is the increase of yield of the raw meat, which can provide benefits to the producer and the consumer [1]. Beneficial effects of marination on meat texture include a juicier texture and reduction of water loss during cooking.

There are 3 methods for producing marinated products that include immersion, injection, and vacuum tumbling [1]. Immersion, the oldest method, consists of submerging the meat in the marinade and allowing the ingredients to penetrate the meat through diffusion with the passage of time. This method is unreliable for the meat industry because it does not provide regularity in distribution of the ingredients, and it is not practical because it requires long processing times and limits the quantity of marinade to be added [1].

Multineedle injection marination is perhaps the most widely used method because it allows for dosing an exact quantity of the marinade, ensuring regularity in the products without the time losses required for immersion [1]. To inject a marinade, needles or probes are inserted, and the marinade is injected as the probe or needles are withdrawn, spreading the marinade throughout the piece [2].

Vacuum tumbling is a method of marinating poultry meat to provide a ready-to-cook, value-added product at either the food processing plant

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or the supermarket or butcher shop. Massaging and tumbling result in the extraction of protein exudates (consisting mainly of the salt-soluble proteins actin and myosin), which promote cohesion during thermal processing. Tumbling yields products with improved juiciness and better slicing characteristics. Studies report that extraction of the myofibrillar proteins to the surface of the meat serves 2 functions. First, protein coagulates upon heating to improve binding properties. Second, the extracted protein acts as a sealer when thermally processed, thus facilitating the retention of moisture contained in the meat tissue [3].

SALTS

Two of the most common ingredients in brines and marinades are NaCl and some type of phosphate, most commonly sodium tripolyphosphate (**STP**) [4]. Salt (NaCl or KCl) is one of the oldest and most effective food preservatives used. Salt is included in poultry meat formulations to do the following: 1) enhance product flavor, 2) increase moisture retention, 3) act as a synergist with STP to extract salt-soluble proteins, 4) inhibit the outgrowth of *Clostridium botulinum* via the synergistic role of salt with sodium nitrite (cure), 5) dehydrate the meat and serve as a preservative when applied at high concentrations to the surface of meat [5].

Because salt easily dissolves in water, the ionic strength of the water increases. Poultry meat contains approximately 70% water, which is ionic in nature due to the monovalent minerals present in muscle tissue as soluble salts and the ionized forms of these salts (e.g., cations: Na^+, K^+, and anions: Cl^-, S^-) [6]. However, the ionic strength of the muscle tissue fluid is lower than that of brine, and through the process of osmosis, the brine solution will be absorbed by the meat until a state of equilibrium is reached. Salt content of a meat product is not a regulated ingredient but is self-limiting, because high concentrations will negatively affect the palatability of the product. Typically, finished brined poultry meats and products will contain approximately 2% salt on average. Depending on the products, salt levels can range from 1.5 up to 3%. Because of dietary restrictions on salt intake, ingredients such as KCl (0.75% in a 60:40% NaCl-KCl combination), phosphates, and other high ionic strength compounds can help increase water-holding capacity (**WHC**) while maintaining low levels of salt. However, KCl is not readily used in further-processed products because it can lead to astringent off-flavors in the product [7]. In addition to salt levels, purity of the salt is also important, because impure salts may interfere with quality of the product.

WHC

Although salt increases meat tenderness, the state of the myofibrillar proteins will determine how effective the salt will be with improving meat characteristics [8]. The most important myofibrillar proteins associated with meat quality characteristics and water binding are actin (thin filament), myosin (thick filament), and their combined structure actomyosin, which are found in the salt-soluble fraction. Salt-soluble (>0.4 *M*) proteins make up approximately 50 to 55% of the total myofibrillar proteins. Salts function by unfolding myofibrillar proteins and solubilizing them in saltwater solutions. Myofibrillar proteins unfold due to electrostatic repulsion of the Cl^- ions, and charged binding sites are exposed [9]. In addition to exposing more charged sites where water can be bound, the electrostatic repulsion will increase the space between the thin and thick filaments. Increasing the size of the space between filaments increases the amount of water that can be retained by the muscle. Water occupying this space is referred to as free water and is held there by the steric effect [10]. Free water makes up the majority of water that is retained by meat. Immobilized water refers to water that is also entrapped but is further held by a net charge attraction. Bound water is bound to the ionizable groups of amino acids of the proteins and other groups able to form H bonds. Around 4% of the water is bound to the muscle proteins and cannot be removed; immobilized water accounts for 10 to 15% and can be removed by cooking, and the remaining water is loosely bound or free, which can be lost by processing procedures such as cutting, grinding, and storage. Therefore, anything that influences the spacing between the thick and thin filaments or the ability of the proteins to bind water can affect water-holding properties of the meat.

pH AND WHC

A related factor influencing water binding is meat pH. The rate and extent of pH decline

during rigor development in muscle can influence myofibrillar protein functionality, thereby altering meat tenderness, color, WHC, and meat protein binding ability [11]. As rigor develops, myosin combines with actin to form actomyosin. Actomyosin, although not a poor water binder, is not as good as myosin and not as readily solubilized. Additionally, lactic acid accumulates and muscle pH drops to 5.6 or 5.7 in normal tissue [12]. In broilers, rigor mortis takes 4 to 6 h to complete, and in turkeys, 6 to 8 h. As pH declines during rigor, there is an efflux of fluid from the myofibrillar space caused by the decrease in negative electrostatic repulsion between filaments [13]. As rigor is resolved, the muscle pH approaches the isoelectric point for the myofibrillar proteins, which is approximately 5.1. Decreased WHC occurs because actin and myosin are near their isoelectric point in postrigor meat, and the net charges on the protein will be a minimum, as will space between filaments for water to be held or bound. Furthermore, researchers have reported increased protein functionality from prerigor meat. For example, Xiong and Brekke [14] found greater extractability of myofibrillar proteins from prerigor meat as compared with postrigor meat. Also, the researchers observed that early postmortem meat had increased water retention compared with postrigor meat. Postrigor meat has decreased spacing between filaments and decreased protein functionality; therefore, less free water is retained.

Decreased WHC is even more evident in meat from animals that have accelerated postmortem metabolism after slaughter. Research has indicated that the low pH resulting from rapid metabolism early postmortem when combined with high carcass temperatures causes extensive protein denaturation in the muscle, thereby affecting meat quality characteristics [15, 16, 17, 18]. The loss of protein functionality due to extensive protein denaturation is considered to be the primary factor associated with the development of pale, soft, and exudative (**PSE**) meat characteristic [16, 19, 20, 21]. When meat conditions such as PSE meat exist, the WHC and other meat quality characteristics are further compromised because of the extensive protein denaturation. Differences in WHC, brine pickup, and retention have been reported to vary with fillet color and initial fillet pH [22, 23]. Alvarado and Sams [22] and Woelfel and Sams [23] compared brining and WHC of broiler breast fillets characterized as "pale" fillets to fillets characterized as "normal." Their findings suggested that the fillet color and pH were highly correlated with WHC and percentage of brining pickup and retention. Fillet characterized as lighter in color had an initial lower pH, lower brine pickup, and higher drip and cook loss compared with fillets that were characterized as dark. In general, at a meat (beef and pork) pH below 4.5 and above 10, irreversible changes occur affecting decreased protein functionality and decreased WHC [12]. The water lost due to irreversible loss of protein functionality includes free, immobilized, and bound water. Therefore, it should be noted that in meat with extensively denatured proteins, such as PSE, brines or marinade ingredients cannot overcome all of the lost protein functionality.

PHOSPHATES

Phosphates vary in their solubility and effect on muscle pH, but generally, alkaline phosphates improve water retention by shifting the pH further away from the isoelectric point of the myofibrillar proteins and by unfolding muscle proteins, thereby exposing more charged sites for water binding [24]. Additionally, actomyosin bonds in postrigor meat are cleaved by phosphates, thereby increasing the potential for swelling of the filaments [25]. Phosphates are able to shift pH due to their buffering capacity. Typically, short-chain phosphates such as orthophosphates and pyrophosphates have the best buffering capacity, whereas the longer chain phosphates have less buffering capacity; therefore, the percentage of diphosphate or pyrophosphate will determine the strength of the buffering capacity. Depending on the type of phosphate used, pH of the solution can be increased or decreased. Acid phosphates include monosodium phosphate, monoammonium phosphate, and sodium acid pyrophosphates, whereas alkali phosphates include di- and trisodium phosphates, STP, and tetrasodium phosphate. Acid phosphates would typically be used in marinades in which the solution pH is low. Because low pH tends to decrease water binding, alkaline

phosphates would be more likely used in marinade solutions to maximize WHC.

When phosphates are used for increasing water-holding properties of meat, the USDA requires that phosphate concentrations are no higher than 0.5% of the finished product weight. Although there are many phosphates to choose from, STP remains the most commonly utilized in brine solutions because it is easy to use and inexpensive. Sodium tripolyphosphate accounts for approximately 80% of the phosphates used in further-processed meat products. Other commonly used phosphates include sodium pyrophosphate and sodium hexametaphosphate (**SHMP**). Alkaline phosphates such as STP serve to increase WHC, increase cook yield, extract muscle proteins, reduce oxidative rancidity, preserve meat color, increase flavor retention, and reduce microbial growth [26].

The most functional phosphate is pyrophosphate; however, the solubility index is low. For this reason, longer-chain STP is commonly used, and blends of phosphates are used to optimize solubility and functionality. When added to water, STP is hydrolyzed, forming the functional diphosphate. Pyrophosphates are a more soluble form of diphosphates and are therefore easier to use. In poultry products, sodium pyrophosphates and STP have been shown to enhance the WHC and salty taste in frankfurters formulated with reduced salt levels by 20 and 40% [27].

Tetrasodium phosphates produce good binding ability because of their high pH (approximately 11), whereas sodium acid pyrophosphate decreases pH, and as a result, decreases WHC and yield. Also, tetrasodium pyrophosphate allows for the greatest bind in emulsion products but has a pH of 11, which can be caustic. Furthermore, tetrasodium phosphate begins to create a soap when combined with fats [24]. In contrast to high-pH phosphates, sodium acid pyrophosphate is acid in nature and has poor water-binding properties compared with the alkaline phosphates. Additionally, in curing systems, acid phosphates can lead to off-color because of rapid curing.

Today, blends are becoming more popular based on their solubility and functionality in a variety of meat product formulations. Sodium SHMP is a water-soluble form of sodium phosphate that is also known as Graham's salt. However, the solubility of SHMP is not as good as other tripolyphosphates, so the phosphate can be blended with others, giving better solubility properties. For example, blends including SHMP combined with tripolyphosphate improve the solubility of SHMP. Desirable properties for blends include proper alkaline pH, good solubility, ability to hydrolyze to form diphosphate, Ca compatibility, the ability to solubilize myofibrillar proteins, and the ability to expose charged binding sites to increase WHC [28].

In poultry, research indicates that when poultry meat is injected with a solution of sodium phosphate, there is no difference in fillet tenderness between aged fillets (16 h) and fillets marinated but not aged (deboned 3 h postmortem) [29]. In this study, the whole birds were postchilled and aged for 16 h while the marination time without aging was 3 h. Moreover, Zheng et al. [30] compared the functionality of tetrasodium pyrophosphate, STP, and hexametaphosphate on poultry breast fillet moisture pickup and retention. Their results indicated that tetrasodium pyrophosphate-treated breast fillets had the highest yield, whereas STP had similar effects on purge. They also concluded that SHMP had the highest moisture pickup but the lowest retention. Alvarado and Sams [22] investigated using salt and phosphate as a remediation for PSE broiler breast meat. Regardless of the phosphate marinade treatment, moisture binding or retention properties of the PSE meat were not restored to the level of the control group. However, Gorsuch and Alvarado [31] determined that marination with high-pH phosphates (~pH 11) can reduce the undesirable characteristics of poor-quality meat (such as PSE meat) without altering flavor, increasing the development of oxidation, or reducing shelf life.

Many phosphates are not easily soluble in most salt marinade solutions; therefore, phosphates are typically dissolved in room-temperature water before adding salt and then chilled before use. Some new blends of phosphates on the market have increased solubility regardless of the addition of salt. Some of the new commercial blends of phosphates do not need to be put into solution before salt because of modifications that make them more soluble. Excess phosphate addition can cause "soapy" flavors, rubbery texture, and poor color [5].

Although phosphates possess very functional properties in poultry meat systems, lately consumers have perceived phosphate use as a negative. Other additives that have been utilized as phosphate replacers include sodium citrate and carageenans to increase water-holding properties. Low-sodium, phosphate-free products tend to be formulated by increasing the amount of protein, particularly nonmeat proteins, or by decreasing the amount of water that is added [32]. Several additives, for example, sodium citrate, and other ingredients have been used in phosphate-free meat products to enhance their WHC.

CONTROL OF *LISTERIA MONOCYTOGENES* BY MARINATION WITH ORGANIC ACIDS

Acid marinades are becoming more popular as antimicrobial ingredients; particularly, for their ability to reduce *L. monocytogenes* in ready-to-eat meat products. Typical marinades utilized for their antimicrobial properties include sodium lactate, potassium lactate, sodium citrate, sodium lactate combined with sodium diacetate, and combinations of sodium lactate with potassium lactate and diacetate. Sodium lactate levels regulated by the United States are 2.9% pure sodium lactate or 4.8% when using a 60% lactate solution in cooked poultry products [5]. When formulating with sodium lactate, salt concentration would likely need to be reduced, because the sodium lactate enhances the salty flavor. According to US regulations, sodium acetate and diacetate are approved as flavoring compounds at a maximum level of 0.25% of the formulation weight [5]. Research has shown that sodium lactate in cooked strained beef and beef roasts and sodium diacetate in turkey slurry reduces the growth of *L. monocytogenes* [33]. However, during refrigeration, there are surviving *L. monocytogenes* organisms that increase in numbers. Cooked chicken treated with lactate and dipped into a *L. monocytogenes* cocktail is shown to have a longer lag phase compared with the control [34]. However, *L. monocytogenes* growth still occurs during refrigerated storage. In general, sodium lactate and diacetate are thought to inhibit bacterial growth by extending the lag phase [34].

Although acid marinades may act as antimicrobials, they also affect meat quality and functionality. Traditionally, acid marinades were used to improve the flavor and texture of prepared meats during storage. Whereas alkali salt-phosphate marinade systems serve to increase WHC and tenderize meat, acidic marinades that are highly acidic (pH below 5.0) tenderize the meat by denaturing proteins, but the marinades do not improve WHC to the extent of alkali marinades. Most of the time, salt and acid phosphates are used in combination with acid marinades to help with marinade retention. Other meat quality characteristics have been examined in stored products formulated with acid marinades. Specifically, Carroll [35] found that acidic marinades resulted in poor bind ability and reduced moisture retention following cooking in turkey deli loaves. In another study, cooked cured ham products were formulated with varying levels of sodium lactate, sodium diacetate, or buffered sodium citrate. When comparing the different ham formulation for appearance, internal color, structure, and firmness, only minor differences were observed. However, the addition of 0.2% sodium diacetate had a negative effect on the odor and taste of the ham product [36].

Sodium lactate is added frequently to meat and poultry products. It is available as a 60% aqueous solution; levels of 2 to 3%, based on final weight, are recommended as a flavor enhancer in fresh and cooked meat and poultry products. The sodium lactate solution, which has a pH of 6.8 to 7.0, is used as a pH control agent, and additions of 2 to 4% do not alter the meat pH. Lactate has been reported also to be effective as a firming agent and humectant [37]. Suppressed microbial growth has been reported in meats formulated with sodium lactate. According to a study conducted by Bacus and Bontenbal [38], a concentration of 4% sodium lactate in frankfurters or chicken rolls inhibited *L. monocytogenes* growth during refrigerated storage, and lactate addition also reduced aerobic plate counts in the products.

According to Samelis et al. [39], after the 1998 to 1999 *L. monocytogenes* outbreak involving meat products, the USDA Food Safety and Inspection Service announced increases in the permissible levels in meat products for sodium

lactate, sodium acetate, and sodium diacetate to 3 [4.8% of the commercially (60% wt/wt) available compound], 0.25, and 0.25%, respectively. Research showed that the single use of each antimicrobial in the formulation at these levels provided inhibition of surface-inoculated (3 to 4 log cfu/cm^2) *L. monocytogenes* ranging widely from 20 to 70 d between treatments of vacuum-packaged frankfurters stored at 4°C. Sodium lactate at 3% and sodium acetate at 0.25% were the most and least effective additives, respectively, whereas sodium diacetate at 0.25% was intermediate in anti-*L. monocytogenes* effectiveness.

Potassium lactate functions in a similar manner as sodium lactate but is less preferred because of its slightly bitter taste. Potassium lactate is soluble in water and available as a 60% aqueous solution [40]. Effects of lactate salts on sterile strained chicken or beef were examined by Shelef and Yang [41]. A concentration of either the sodium or potassium salts suppressed growth of *L. monocytogenes* in sterile chicken or beef, causing an extended lag phase of 1 to 2 wk at 5°C.

These findings indicate that the levels of lactates and acetates permitted by the USDA Food Safety and Inspection Service may be insufficient to control growth of *L. monocytogenes* throughout the commercial shelf life of cured meat products, which is expected to be 75 to 90 d; thus, increases in these concentrations may be needed. However, by incorporating combinations of chemical and other antimicrobials in the formulation, antilisterial properties can be achieved. Also, additional treatments, such as spraying or dipping products in antimicrobial solutions before packaging, and postpacking pasteurization can be combined to enhance the effectiveness of chemical additives. In addition to the potential for providing increased anti-*L. monocytogenes* effects, combinations of antimicrobials or treatments may lessen any negative effects on the sensory quality of cured meat products [39].

Acetic and lactic acids are among the most widely used as preservatives. The antimicrobial effects of organic acids such as propionic and lactic is due to both the depression of pH below the growth range and metabolic inhibition by the undissociated acid molecules. According to Buchanan et al. [42], many investigators have observed that when *L. monocytogenes* is placed in an acidic environment that does not support growth, the organism will be inactivated over time. It has also been observed that under nonideal pH conditions that still support growth, the organism will tend to decline after reaching stationary phase, particularly at elevated incubation temperatures. The inhibition or inactivation of *L. monocytogenes* is enhanced when organic acids are used as acidulants. Sufficiently high levels of organic acid salts such as sodium lactate and sodium acetate can inhibit or inactivate the pathogen, even at neutral pH level. Various investigators have concluded that the rate of inactivation is dependent not only on the pH of the environment but also on the identity and concentration of the acidulant used to modify the pH [42].

According to Sorrells et al. [43], at 10, 25, and 35°C, acetic and lactic acids were more inhibitory against *L. monocytogenes* than citric acid and hydrochloric acids. Conner et al. [44] also reported that acetic and lactic acids were the most inhibitory in media. Many investigators have studied and reported the inhibitory effects on low pH and organic acids on *L. monocytogenes*. Two inhibitory mechanisms have been proposed: 1) an intracellular acidification (loss of homeostasis) and 2) a specific effect on the acid (nondissociated form) on metabolic activities. Ita and Hutkins [45] observed that low cellular pH was not the major factor in the inhibition of *L. monocytogenes* at acid pH; cells treated with organic acids at pH values as low as 3.5 were able to maintain their cytoplasmic pH at a value near 5. Therefore, the efficiency of the treatments using organic acids would be due to the nondissociated fraction rather than to proton toxicity.

The inhibitory effect of these acids can be correlated with their dissociation constant ($\mathbf{pK_a}$) and with the greater permeability of the cell membrane to weak acids in their undissociated form. Hydrochloric acid is totally dissociated in aqueous environments, whereas acetic acid ($pK_a = 4.76$) has the highest concentration of undissociated acid, and lactic acid ($pK_a = 3.86$) has the lowest. Acetic acid is more efficient against *L. monocytogenes* than a stronger hydrochloric acid used at the same pH. The

highest inhibitory effect of acetic acid can be explained by its ability to diffuse through the cell membrane, which is permeable to nondissociated, nonprotonated, and lipophilic weak acids. This leads to an accumulation of the acid within the cell cytoplasm, acidification of the cytoplasm, disruption of the proton-motive force, and inhibition of substrate transport [46]. However, lactic acid may be less inhibitory, because it cannot passively penetrate the cell membrane. The results of Buchanan et al. [42] observed that neutral pH values indicate further that the reported anti-*L. monocytogenes* activity of sodium lactate and sodium acetate remains attributable to the undissociated acid and argues against alternative hypotheses of separate inhibitory mechanisms at higher pH values. This implies that increases in anti-*L. monocytogenes* activity can be expected if the pH of an acetate- or lactate- containing system is decreased even to a small extent such that is was closer to the pK_a of the acid.

CONCLUSIONS AND APPLICATIONS

1. Marination of poultry meat products can be used effectively to increase yield and improve texture.
2. Marination of poultry products with acid marinades can be used to control *L. monocytogenes* growth.
3. Continued research with acidic marinades is needed to determine further effects on product quality and control of other pathogens.

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